

BIOFILTRATION FOR CONTROL OF HYDROGEN SULFIDE

BY

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To my father for making this possible
and
In memory of my mother

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A laboratory scale biological filter system for control of hydrogen sulfide (H_2S) emissions has been developed and optimum design and operating parameters are evaluated. This biofiltration system uses yard waste compost as filter material, and the performance of the system for controlling waste gas containing H_2S is evaluated through long term operation.

Extensive tests have been conducted to determine the effect of various filter bed operating parameters such as pH, temperature, pollutant retention time, pressure drop, water content, etc. on H_2S removal efficiencies.

A biofilm model is used to characterize the macro-kinetics of the biofiltration process. Models for the kinetics of H_2S oxidation are developed that allow one to quantitatively predict the performance of the biofilter.

Decomposition of composts under aerobic conditions and the effect of H_2S concentrations on the decomposition rate are quantitatively determined. The half life time for the composts tested is estimated to be between 3.3 and 6.1 years.

Hydrogen sulfide loading rate and maximum H_2S elimination capacity of the filter material are emphasized as important design parameters. The maximum H_2S elimination capacity of a typical yard waste compost is determined to be $130 \text{ g-S/m}^3\text{-hr}$ under optimized conditions.

Hydrogen sulfide is oxidized to sulfuric acid in the biofilter system, where biological oxidation plays a major role. Acidification of the biofilter system and accumulation of sulfate in the filter material are determined to be natural features of the oxidation process, where the latter is toxic for biological activities of the microorganisms. Appropriate methods have been developed to effectively mitigate this affect.

System 'upset' is identified as being due to compost dry-out and system overloading. Methods have been identified to provide for recovery of the defective filter material.

Operation of a full scale biofilter system at a wastewater treatment plant has been investigated. Both the laboratory and full scale systems have demonstrated excellent performance over substantial operational periods. Hydrogen sulfide removal efficiencies of 99.9+% have been constantly achieved when the H_2S inlet concentrations are varied from 5 to 2650 ppmv.

CHAPTER 1 INTRODUCTION

Hydrogen sulfide (H_2S) is a highly toxic air pollutant which has been identified in the list of 190 air toxic substances in Title III of the 1990 Amendments to the Clean Air Act.

Considerable amounts of H_2S are produced in association with industrial processes, such as petroleum refining, rendering, waste water treatment, paper and pulp manufacturing, food processing, and in the treatment of "sour" natural gas and other fuels. Hydrogen sulfide is frequently the main component of most observable odorous emissions.

Hydrogen sulfide is an odorous gas, and its presence at low concentrations is easily perceived and recognized due to its characteristic odor of rotten eggs. Hydrogen sulfide is perceptible to most people at concentrations in excess of 0.5 parts per billion (ppb) in air. Control of H_2S emissions is essential to protect public health and welfare as well as to mitigate vegetation and material damage problems.

Numerous processes involving physico-chemical principles have been developed in order to effectively remove hydrogen sulfide from air, waste gases and liquids

(Bethea et al., 1973; Ferguson, 1975; USEPA, 1985; Lalazary et al., 1986; Walker et al., 1986; Lindstrom, 1990). Processes that have been used to remove H_2S from waste gas streams involve either physical treatment or chemical oxidation. Some methods require addition of chemicals, and energy expenditure is usually necessary for physical treatment. Additional environmental problems are encountered with chemical additions, where resulting products and by-products require further treatment and disposal.

Biofiltration can provide for a universal, simple, economically feasible, and efficient pollutant-destructive control technology for a variety of toxic and hazardous substances in waste gas streams. In recent years biological filters have been developed and described which have the potential to simply and effectively control odors, including H_2S emissions (Prokop and Bohn, 1985; Allen et al., 1987a; Eitner and Gethke, 1987; Hartenstein, 1987). Deodorization methods based upon the activity of microorganisms are beginning to attract increasing attention in the U.S.

Although the biofiltration technique has been shown to be an efficient, practical and simple gas cleaning technology, which is increasingly being used around the world, the design and operation parameters as well as the microbial processes involved have not yet been very well defined. In particular, little research has been directed at the details of the biofiltration control of H_2S . A

systematic compilation of data from an operational point of view is also lacking. Most designs are conservatively based on blanket 'rule of thumb' criteria (Forster and Wase, 1987). The performance of biofilter systems, therefore, is not readily predictable and sometimes these systems are not operated under suitable conditions. As a result, the desired odor control efficiency is sometimes not achieved (Allen et al., 1987b). It is essential that more work be done to demonstrate the effectiveness of these systems in order to support further progress in the use of biofiltration as well as to develop better biofilters, based on an understanding of the fundamental physical, chemical and biological processes involved.

A major disadvantage of biofiltration technology is the limited degradation capacity represented by the volume of waste gas treated per unit area of filter material per unit time ($\text{m}^3/\text{m}^2\text{-hr}$). This limitation restricts the applicability of biofiltration systems to handling dilute waste gas streams and requires the filter bed to be large in order to handle high volumetric gas flows.

In order to overcome the uncertainties and disadvantages encountered in the full scale application of biofiltration technology, an exhaustive study is necessary for the application of biofiltration technology to control the emissions of air pollutants.

The objectives of the proposed research were to develop a quantitative knowledge of the principle and operation of

a microbial biofilter system for removal of H_2S from waste gas streams and determine the operating parameters necessary to optimize the performance of such a biofilter system.

The objectives were achieved through the following studies:

1. Evaluation of the properties of filter materials and their decomposition characteristics under aerobic conditions.
2. Evaluation of the effects of design and operational parameters on H_2S removal efficiencies on laboratory scale biofilter systems. Variables evaluated included temperature, pH, compost water and sulfate content, H_2S elimination capacity, pollutant retention time, etc..
3. Determination of the predictive relationships for H_2S control efficiencies through chemical kinetic studies.
4. Evaluation of system performance and determination of optimum maintenance procedures for biofiltration control of H_2S during long term operation.
5. Evaluation of the field performance of a full scale biofiltration system for control of H_2S emissions at a local waste water treatment plant.

The research reported here focuses mainly on the utilization, improvement and optimization of a compost biofiltration tower system. Optimization of this system has been directed toward the best achievable control of

hydrogen sulfide. This research provides a detailed data-base on the effects of system variables on H_2S control efficiency, which provide for optimization of design and operating conditions.

CHAPTER 2 BACKGROUND

Properties of Hydrogen Sulfide and Regulations

Physical and Chemical Properties

Hydrogen sulfide is a colorless gas that has a foul rotten egg odor and is slightly heavier than air. Hydrogen sulfide is moderately soluble in water. The solubility of H_2S decreases with increasing temperatures. Figure 2-1 shows the solubility of H_2S as a function of temperature.

Dissolved H_2S dissociates in accordance with the following reversible ionization reactions:



The distribution of the above species as a function of pH is shown in Figure 2-2. It is apparent from Figure 2-2 that the concentration of HS^- species is insignificant when pH values are less than 6. The latter condition is normal in a biofilter system for control of H_2S . S^{2-} , on the other hand, may not occur at all.

Hydrogen sulfide can serve as a reducing agent, reacting with sulfuric acid (H_2SO_4) to form sulfur dioxide (SO_2) and elemental sulfur (S^0) (Greyson, 1990):

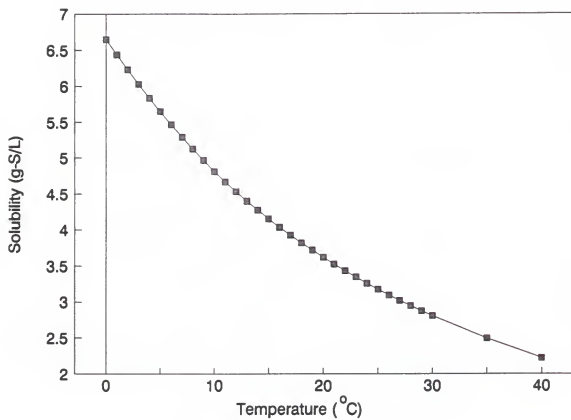


Figure 2-1. Solubility of H₂S in water at 1 atm.
Data adopted from Piscarczyk, 1982.

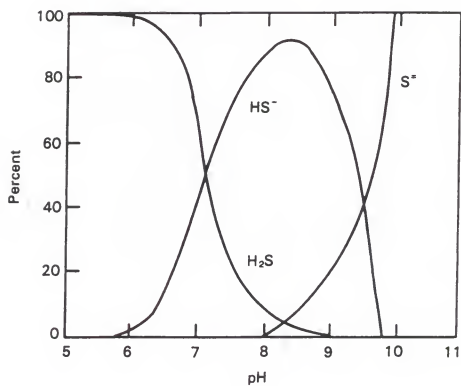
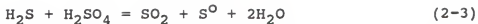


Figure 2-2. Effect of pH on H_2S equilibrium.
Source: Sawyer, 1967.



Hydrogen sulfide also burns in air to form sulfur dioxide and water:



Table 2-1 summarizes the physical and chemical properties and the odor threshold of H_2S .

Toxicity of H_2S

Hydrogen sulfide is almost as toxic as hydrogen cyanide (HCN), which is used in prison gas chambers (Parker, 1977). Human exposure to small amounts of H_2S in air can cause headaches, nausea, and eye irritation, and higher concentrations can cause paralysis of the respiratory system, which results in fainting and possible death. Concentrations of the gas approaching 0.2 percent (2000 ppmv) are fatal to humans after exposure for a few minutes (NRC, 1979).

Hydrogen sulfide has a characteristic rotten egg smell at low concentrations. But as levels of H_2S increase, a person's ability to sense dangerous concentrations by smell is quickly lost. If the concentration is high enough, unconsciousness will come suddenly, followed by death if there is not a prompt rescue.

The Occupational Safety and Health Administration (OSHA) has established limits for work place exposure to H_2S

Table 2-1. Physical and Chemical Properties of H₂S^a.

Molecular Weight	34.08
Boiling Point, °C	-60.2
Melting Point, °C	-83.8 to -85.5
Vapor Pressure, -0.4°C	10 atm
25°C	20 atm
Specific Gravity (Relative to Air)	1.192
Auto Ignition Temperature, °C	250
Explosive Range in Air, %	4.5 to 45.5
Odor Threshold, ppbv	0.47

^a Source: USEPA, 1985.

at 20 ppm (15-minute exposure) for an acceptable ceiling concentration and 50 ppm for a maximum exposure during an 8-hour work shift if no other measurable exposure occurs. The National Institutes of Occupational Safety and Health (NIOSH) established an H_2S exposure level at 10 ppm (10 minutes) as a maximum permissible limit (once per 8-hours shift), with continuous monitoring required where H_2S concentrations could equal or exceed 50 ppm or greater (NIOSH, 1979).

Hydrogen sulfide is an explosive gas. The lower and upper explosive limit are 4.5 and 45 percent in air by volume, respectively.

Hydrogen sulfide can attack materials and cause discoloration and tarnishing. Materials commonly affected are paint, copper, zinc and silver (Painter, 1974).

Sources of H_2S Emissions and Regulations

Natural emissions are mainly caused by biological decay of protein materials. The natural global rate of emission is estimated to be about 84 Tg/year (Urone, 1986).

Anthropogenic emission sources include petroleum refining, natural gas plants, sewage treatment facilities, coke ovens, Kraft paper pulp plants, and waste disposal sites. There are no federal U.S. emission standards for H_2S at present, nor are there federal ambient air quality standards for this gas, but a number of states have

established independent standards for H_2S emissions. These states, which include California and New Mexico (10 ppm), and Ohio and Michigan (1670 ppm). California, Kentucky, Minnesota, Montana, New Mexico, New York, North Dakota and Pennsylvania also have air quality standards for H_2S . The standards vary from 0.003 ppm for New Mexico to 0.1 ppm for Pennsylvania, whereas and most of the other states specify a standard of 0.03 ppm (Urone, 1986).

Since H_2S is a highly toxic air pollutant, H_2S has been identified by the USEPA as one of 190 air toxic compounds in Title III of the 1990 Amendments to the Clean Air Act. In view of the wide spread exposure to this pollutant, emission and air quality standards for H_2S are going to be set in the near future by EPA.

Biofiltration as a Air Pollution Control Technology

Biological degradation is widely used for treatment of liquid and, to a lesser extent, solid wastes, but has received little attention as a means of controlling emissions of industrial gaseous wastes. Biofiltration is a relatively new technology for control of air pollutants, in which the air contaminants from off-gas streams are biologically removed in a solid biological reactor. While it is a well established air pollution control technology in European countries, biofiltration as an air pollution control technology has received little attention and application in the United States. Few environmental

professionals in this country appear to be aware of the 'biofiltration' process and its applications.

Although there are some applications of biofiltration in the U.S. and some technical papers have been published in the English language, most of the research and development work on biofiltration has been conducted in Europe and the majority of the recent research data have been published in the German language. Excellent reviews of previous biofiltration work have been published by Hartenstein (1987), Leson and Winer (1991), Ergas et al. (1991), and Dharmavaram (1991).

History and Development

The first deodorization method based upon the use of a soil bed in the U.S. was developed and patented by Pomeroy in 1957. Later, Pomeroy (1982) described the deodorization of waste gases emitted from sewer lines by a soil bed system used in Los Angeles in 1957. The microbiological degradation of sulfur-containing gases in the filter bed was observed to be effective in these studies.

Other early applications of biological treatment of odorous gases include a soil bed system built in Nurnberg, West Germany, in 1959 and biofilters built in Geneva, Switzerland, and Mercer Island, Washington, to remove odors from wastewater treatment and compost manufacturing, respectively, in the mid-1960s (Bohn and Bohn, 1987).

Additional studies in the US have been carried out by Carlson and Leiser (1966), Bohn and Miyamoto (1973), Bohn (1975, 1976, 1977, 1989), Pomeroy (1982), Prokop and Bohn (1985), Hartenstein and Allen (1986), Bohn and Bohn (1986, 1988), Hartenstein (1987), and Allen et al. (1987a, b, c; 1989).

In spite of the work mentioned above, most of the research and development in biofiltration technology has been carried out in Europe, especially in West Germany and Holland. In the latter countries the principle of biofiltration has been applied to a wide variety of environmental problems. Among the many researchers in the field, Ottengraf and coworkers in Chemical Engineering Department, The Eindhoven University of Technology, Holland, have contributed most of the theoretical research in biofiltration in a series of papers which have been published in the English language (Ottengraf, 1977; Ottengraf and Van Den Oever, 1983; Ottengraf et al., 1984; Ottengraf, 1986; Ottengraf et al. 1986; Ottengraf, 1987). Also, Eitner in West Germany, has made significant contributions to the research and development of biofiltration (Eitner and Gethke, 1987), although most of his publications are in the German language (see Hartenstein, 1987; Leson and Winer, 1991).

The practice and application of biofiltration has also been reported in other countries such as Japan (Terasawa et al., 1986), New Zealand (Rands et al., 1981) and Canada

(Rotman, 1991a).

At present, biofiltration is considered to be a state-of-the art technology for odor removal in West Germany, and it has been estimated that 40% of deodorization facilities at wastewater treatment plants are biofilters (Frechen and Kettern, 1987).

Applications

The first systematic study of odor control using biofiltration in this country was conducted by Carlson and Leiser (1966). They studied the removal efficiencies of sewage odors using a laboratory scale soil bed. Using hydrogen sulfide as the test gas, a 99% removal efficiency was achieved, and biodegradation was reported to be the primary removal mechanism.

Prokop and Bohn (1985) reported that a soil bed system for control of rendering plant odors had been in operation since September, 1983. The soil bed treats 1100 m³/h of cooker non-condensable waste gases using a bed surface area of 420 m². In this work an odor removal efficiency of 99.9% was obtained.

Rands et al. (1981) reported that a full-scale compost filter system was constructed in 1978 at Moerewa, New Zealand, to treat odors from a rendering plant. The system was designed to treat 900 m³/h of air containing hydrogen sulfide concentrations up to 1000 parts per million (ppm) by volume. An average H₂S removal efficiency of 99.9% was

observed.

Allen et al. (1987a, b, c) investigated a compost based tower biofilter system used for odor control in a wastewater treatment plant. The odor-causing compounds identified were reduced sulfur compounds such as H_2S , methyl mercaptan, dimethyl sulfide and dimethyl disulfide as well as terpene hydrocarbons. Removal efficiency for total reduced sulfur compounds (TRS) was 65 to 72%. The poor performance of this system was determined to be the short residence time in the system, poor gas distribution, and improper maintenance.

Biofiltration control of volatile organic compounds (VOCs) has been reported by Ottengraf (1986), Kampbell et al. (1987), Bohn (1989), Paul and Castelijns (1987), and Hack and Habets (1987).

In recent years, increasing numbers of biological filters are being used around the world for odor control. It has been estimated that more than 500 biofilters are currently operating in Europe (Leson and Winer, 1991). Excellent summaries of recent applications have been provided by Bohn and Bohn (1987) and Rotman (1991b).

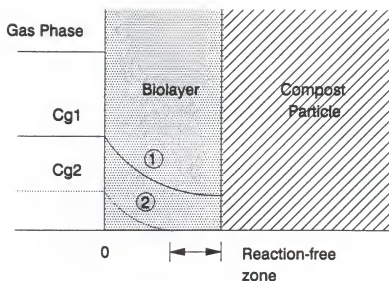
Theoretical Basis

The concept of a biological-film or 'biofilm' is frequently used to describe degradation processes in aqueous systems (Williamson, 1973; Williamson and McCarty, 1976a, b; Jennings et al., 1976; Rittmann and McCarty, 1978). This concept has been adopted and improved to describe the

biofiltration processes (Ottengraf, 1986; Hartenstein, 1987; Paul and Castelijns, 1987; Van Lith, 1989). In particular, Ottengraf and coworkers have carried out systematic studies delineating the overall process and have presented sufficient experimental data to support the proposed model.

In biofiltration, evenly distributed waste gases are forced through a biologically active material, such as soil, peat or compost. Many of the pores of the filter material particles are filled with water. Microorganisms are attached to the particle surfaces to form a layer of film. This wet, biologically active layer surrounding the particles is called a biofilm. The biophysical model proposed by Ottengraf for the biofilm is shown in Figure 2-3. The mechanism of the biological process is derived from a combination of physical, chemical and biological processes that occur in the filter material and is related to two processes in particular; sorption and regeneration. As waste gases pass through the countless narrow pores of the filter material, air contaminants as well as oxygen will adsorb on the surfaces of the pores and dissolve in the liquid phase of the wet biofilm. The absorbed and adsorbed gases are quickly degraded by the biofilter's enormous microbial population. In this way a concentration gradient is created in the biofilter, which maintains a continuous mass flow of the component from the gas to the wet biofilm.

Activity of the biofilter depends mainly on the population of the microorganisms. Soil biofilters can



C_{g1} = High concentrations of air pollutants.
 C_{g2} = Low concentrations of air pollutants.

Figure 2-3. Biophysical model for the biological filter bed. The concentration profiles shown in the biofilm refer to: 1) Reaction limitation, 2) Diffusion limitation. (Source: Ottengraf, 1986, p. 436).

contain 1 billion bacteria, 10 million actinomycetes and 10,000 fungi per gram of soil (Bohn and Bohn, 1987). The role of these microorganisms is to oxidize combined carbon, nitrogen and sulfur to carbon dioxide, nitrogen and sulfate, respectively, before the compounds leave the bed. The air contaminants are, therefore, effectively removed from the waste gas streams.

For good engineering design and environmental decision making, it is essential to understand the mechanisms involved and to reliably predict the kinetics of the biological reactions taking place in these biofilter systems. Many general kinetic models have been developed to predict the behavior of bioreactions in a biological film, none of these models, however, is specific enough to explain the biodegradation of hydrogen sulfide in a biofilter system.

Jennings et al. (1976) developed a mathematical model to predict the percentage removal of a pure, non-adsorbable, biodegradable substrate in a submerged biological filter using the non-linear Monod expression for the substrate utilization rate. In their model, the authors start from a biological slime layer coating a spherical particle. The slime layer is in turn surrounded by a liquid boundary layer. They concluded that even at relatively high values of influent substrate concentrations, the biological removal of a single substrate follows first order kinetics.

Another model developed by Rittmann and McCarty (1978) is a variable-order model of bacterial-film kinetics which incorporates liquid-layer mass transport, biofilm molecular diffusion and Monod kinetics. These investigators concluded that at low substrate concentrations, the reaction follows first order kinetics, whereas at high concentrations the reaction follows one-half order kinetics.

Based on their biophysical model (Figure 2-3), Ottengraf and Van Den Oever (1983) have developed a mathematical model to describe the kinetics of organic compound removal from waste gases for a biofilter system. The model was developed and tested using a soil bed for the removal of toluene, butylacetate, ethylacetate and butanol. From their experimental results, they concluded that all the carbon sources investigated were eliminated according to a zero order reaction, even at very low concentrations of the substrates.

Kampbell et al. (1987) investigated the biodegradation of propane, isobutane and n-butane by soil biofilter beds. They suggested that at low concentrations the rate of biodegradation was proportional to the concentration of the organic compounds (first order reaction), and at higher concentrations the rate becomes independent of the organic compound concentration (zero order reaction). The degradation kinetics appeared to follow a hyperbolic function:

$$1/V = (1/V_{\max}) + (K_m/V_{\max})(1/S) \quad (2-5)$$

where:

V = the biodegradation rate, mg hydrocarbon/kg soil-h

$V_{\max}$ = the maximum possible biodegradation rate,
mg hydrocarbon/kg soil-h

K_m = an empirical constant, half saturation value, ppm

S = the concentration of organic compound in air, ppm

The values of K_m and $V_{\max}$ can be obtained from a Lineweaver-Burk plot of $1/V$ against $1/S$.

Biological Oxidation of Hydrogen Sulfide

Hydrogen sulfide may be utilized by microorganisms in three different ways: assimilation, mineralization and sulfur oxidation (Atlas and Bartha, 1981; Grant and Long, 1981). However, the rates of uptake of hydrogen sulfide based on the assimilation processes are far too low to achieve reasonably high removal efficiencies from a highly loaded waste gas stream. The most important and efficient way for microorganisms to utilize hydrogen sulfide is by the oxidation of sulfur to gain energy. In this process, relatively large quantities of sulfur are oxidized in order for the microbes to receive sufficient energy. The microorganisms living in the biofilter materials are usually mixed cultures. Various groups of microorganisms, therefore, are involved in the energy conversion process under aerobic or anaerobic conditions. However, the

colorless sulfur bacteria are believed to play the major role and their ability to oxidize reduced inorganic sulfur compounds has been clearly established (Roy and Trudinger, 1970; Kuenen, 1975; Brock and Madigan, 1988).

The oxidation of inorganic sulfur compounds is carried out by a spectrum of sulfur-oxidizing organisms which include 1) obligately chemolithotrophic organisms, 2) mixotrophs, 3) chemolithotrophic heterotrophs, 4) heterotrophs which do not gain energy from the oxidation of sulfur compounds but benefit in other ways from this reaction, and 5) heterotrophs which do not benefit from the oxidation of sulfur compounds. Physiological characteristics of some sulfur-oxidizing bacteria are summarized in Table 2-2.

Options for microbial metabolism of hydrogen sulfide must employ one or more of the following metabolic pathways: 1) aerobic oxidation, 2) anaerobic oxidation, and 3) photosynthetic dissimilation. Biofiltration of waste gases is a process utilizing aerobic conditions in most cases. In aerobic oxidation, sulfur-oxidizing bacteria oxidize H_2S to elemental sulfur or higher oxidation states using oxygen (O_2) as an electron acceptor. The biological steps in the oxidation of various sulfur compounds are summarized in Figure 2-4.

Table 2-2. Physiological characteristics of sulfur-oxidizing bacteria.

	Lithotrophic Electron Donor	pH Range for Growth
<u>Thiobacillus</u> Species Growing Poorly in Organic Media:		
1. <u>T. thioparus</u>	H ₂ S, sulfide, S ⁰ , S ₂ O ₃ ²⁻	6-8
2. <u>T. denitrificans</u>	H ₂ S, S ⁰ , S ₂ O ₃ ²⁻	6-8
3. <u>T. neapolitanus</u>	S ⁰ , S ₂ O ₃ ²⁻	5-8
4. <u>T. thiooxidans</u>	S ⁰	2-5
5. <u>T. ferrooxidans</u>	S ⁰ , sulfides, Fe ²⁺	1.5-4
<u>Thiobacillus</u> Species Growing Well in Organic Media:		
1. <u>T. novellus</u>	S ₂ O ₃ ²⁻	6-8
2. <u>T. intermedius</u>	S ₂ O ₃ ²⁻	3-7
Filamentous Sulfur lithotrophs		
<u>Beggiatoa</u>	H ₂ S, S ₂ O ₃ ²⁻	6-8
<u>Thiothrix</u>	H ₂ S	6-8
Other Genera		
<u>Thiomicrospira</u>	S ₂ O ₃ ²⁻ , H ₂ S	6-8
<u>Thermothrix</u>	H ₂ S, S ₂ O ₃ ²⁻ , SO ₃ ⁻	6.5-7.5
<u>Sulfolobus</u> ^a	H ₂ S, S ⁰	1-4

^a Archaeobacterium.

Source: Brock and Madigan, 1988.

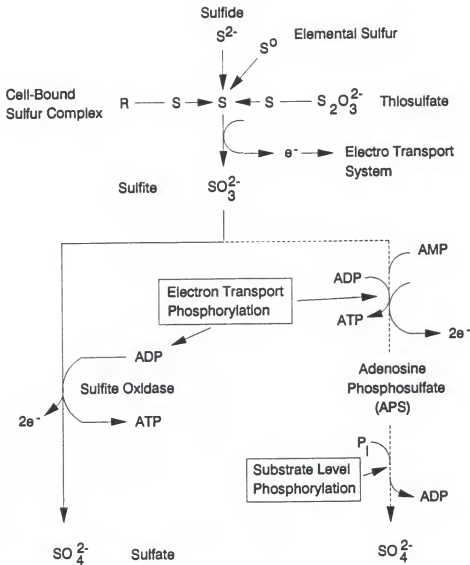


Figure 2-4. Steps in the oxidation of different compounds by *thiobacilli*. The sulfite oxidase pathway is thought to account for the majority of sulfide oxidized. (Source: Brock and Madigan, 1989, p. 704).

CHAPTER 3
FILTER MATERIALS AND THEIR DECOMPOSITION
UNDER AEROBIC CONDITIONS

Introduction

Biofiltration systems or biofilters employ physical, chemical and biological processes such as adsorption, absorption and microbial digestion and oxidative degradation to remove air pollutants from waste gas streams. Microbial degradation and oxidation of the pollutants, however, appear to be the primary removal mechanisms within a biofilter. In the biodegradation process, pollutants are consumed by the microorganisms, providing an energy source or essential nutrients and are converted usually to, less harmful compounds. The filter materials used, on the other hand, must provide the proper environment for microbial growth and contain materials on which the microbes can feed to ensure that the microbial population can develop and survive.

The effectiveness of a biofilter material depends on its physical, chemical and biological characteristics. The lifetime of a biofilter material mainly depends on its rate of carbon (C) and nitrogen (N) mineralization. When available C and N in the filter material are no longer sufficient to support the microbial population in the system, then the material is no longer suitable as a

biofilter. The C or N deficient filter material must be replaced by freshly prepared material and the discarded filter material has to be properly disposed of with due caution for environmental impact. One of the most common options is land application. Determination of the decomposition characteristics of the filter material is, therefore, necessary for usage of the biofilter and eventual land disposal applications.

Considerations necessary for selection of appropriate filter materials and the decomposition of such materials under aerobic conditions are discussed in this section.

Selection of Filter Materials

Effective removal of air contaminants using a biofilter relies on the properties of the filter material, especially the nature and activity of the biomass. The filter material provides the necessary environment for microorganisms to survive, generate, function and allows the entire sequence of biofiltration processes to be carried out. The filter material serves as 1) support material for the microbes, 2) supplemental or alternative nutrient source, 3) moisture storage reservoir, 4) surface area for sorption of air pollutants and interaction between the pollutants and the microorganisms, and 5) a buffer volume for variations in water content and gas conditions during operation (Eitner, 1989). In general, the following factors need to be considered when choosing a suitable filter

medium:

- 1). Density: Too dense material may contain a large fraction of inorganic materials such as stone and sand which are unsuitable as carbon and energy sources for microbial growth.
- 2). Structure: Structure of the medium will affect the uniformity of the filter load. Too large sized materials should be avoided because the surface-to-volume ratio will be reduced.
- 3). Particle Size Distribution: Too small particles affect the pressure drop by compacting and restricting the gas flow.
- 4). Pore Volume (void fraction): This property determines the total surface area available for reaction, also it will affect pressure drop.
- 5). Organic Matter Content: The organic matter controls the microbial population and the useful service life of the filter media.
- 6). pH Value: pH will affect the nature and level of the microbial population and activity.
- 7). Water Retention Capacity: This property will determine the consistency in liquid water content of the filter material, and
- 8). Economics: Reasonable Capital and operating expenditures.

All of these requirements can be met by selecting suitable filter materials. Many kinds of filter materials have been used in biofiltration applications. Examples include field soils, compost, peat, bush, clay, volcanic ash, sand, bark and a combination of such materials (Rands et al., 1981; Prokop and Bohn, 1985; Terasawa et al., 1986 Frechen and Kettern, 1987). The performance of these materials, however, can be very different due to the diversity of their physical and chemical properties. Compost has been considered to be the best choice for filter

materials and has been involved in most applications (Don, 1985; Eitner, 1989), since it provides favorable conditions for supporting microbial populations as well as having superior physical and chemical properties.

The properties of individual composts depend on the materials from which they are derived and the composition of the final product. The filter materials used in this research were mainly yard waste compost and sewage sludge compost or a combination of both. These composts were obtained from different sources and used for different purposes. A general description of the types of composts and their sources are summarized in Table 3-1. The physical and chemical analyses data for the composts listed in Table 3-1 are presented in the corresponding chapters where the use of specific composts is discussed.

Decomposition of Composts under Aerobic Conditions

A number of investigations have been carried out to study the decomposition of anaerobically digested sewage sludges in soils (Miller, 1974; Tester et al., 1977; Terry et al., 1979b; Sweeney and Graetz, 1988; Gale, 1988). Decomposition of fresh and anaerobically digested plant biomass in soil is also reported by Moorhead et al. (1987). Only limited information, however, is available concerning the decomposition of compost. Tester et al. (1977, 1979) stated that the decomposition of compost in soil is not only related to the physical and chemical properties of the

Table 3-1. Description of composts used for this study.

Compost ID#	Source	Description
1	Pompano Beach ^a	Fort Lauderdale sewage sludge compost. Not completely composted. Seven months old when first used (used for decomposition study).
2	Pompano Beach	Two parts yard waste and one part stable cleaning sewage sludge mixed and composted. Seven months old when first used (used for decomposition study).
3	Pompano Beach	Yard trash compost. 13 months old when first used (used for decomposition study).
6	Pompano Beach	25% by volume of sewage sludge compost and 75% of yard trash mixed and composted about 19 months old when first used (used for decomposition study).
12	Kanapaha ^b	Pompano Beach compost similar to Compost #6 mixed with tree bark, yard waste and sewage sludge; lime was used to adjust pH before use. Used in Kanapaha filter bed from 11/20/88. Compost obtained from the filter bed in 5/16/90.
13	Kanapaha	Same as #12, compost obtained and used in Tower #1 from 12/20/90.
13-1	Kanapaha	Same as #12, compost obtained in 2/5/91.
13-2	Kanapaha	Same as #12, compost obtained in 3/20/91.
14	Kanapaha	Yard trash, grass and sewage sludge were mixed and composted; lime was used to adjust pH; about 2.5 years old when obtained and used in Tower #2, 12/20/90.

Table 3-1 -- Continued.

Compost ID#	Source	Description
16	WRR ^C	Yard trash compost, 3.5 months old when first used in Tower #3 from 1/27/91.
17	WRR	1:1 by volume of yard trash and grass composted; about 3.5 months old when first used in Tower #2 from 1/27/91.
17A	WRR	Compost #17 mixed with 2% lime (CaCO ₃), by dry weight of compost. Used in Tower #1 from 1/27/91.

^a Broward County Streets and Highways Division, 1600 NW 30th Avenue, Pompano Beach, FL, 33069.

^b Kanapaha Wastewater Treatment Plant, Gainesville, FL 32602.

^c Wood Resource Recovery, Inc., Gainesville, FL.

compost but also is a function of the particle size of the compost. The decomposition was observed to be directly related to the carbon content in the compost.

Decomposition is affected by a number of environmental conditions, for instance, pH, moisture content, and the presence or absence of foreign chemicals (Miller and Johnson, 1964; Terry et al., 1979a, b; Delaune et al., 1981). In the application of biofiltration to control H_2S emissions, the compost filter material is subjected to conditions that are quite different to that for land applications of compost. In the former case, the compost is exposed to a gas stream which may contain a variety of chemicals, especially H_2S , at various concentrations. The presence of xenobiotics in the gas streams and filter materials could change the population and composition of the microorganisms in the compost or significantly affect their metabolic processes. As a result, the decomposition rate of the compost can be altered. Unfortunately, little information can be found in the literature related to this topic.

The objectives of this study were (i) to evaluate the decomposition of four types of compost by determining the CO_2 evolution, and (ii) to investigate the effect of H_2S at various concentrations on compost decomposition. Such information is valuable for biofilter design and for justifying land disposal applications of the compost after use as a biofilter medium.

Materials and Methods

Four types of compost samples were investigated for their decomposition characteristics during the course of this study. All of the compost samples were obtained from Broward County Streets and Highways Nursery Division, Pompano Beach, Florida. The composts were stored in sealed plastic bags at room temperature (23 ± 2 °C) before use. A brief description of the composts used in this study is presented in Table 3-1 (Composts #1, #2, #3 and #6). The compost samples were analyzed for their physical and chemical properties at the beginning and the end of the investigation. The results of these studies are presented in Table 3-2. Each cured compost was passed through a 10 mm screen to remove larger materials. The compost samples are then placed in 225-mL wide mouth bottles directly for incubation. The experimental arrangement for the decomposition study is shown in Figure 3-1. Four types of compost and one blank, each with three duplicates, were investigated. Compressed air from the laboratory house air supply is controlled to about 4 psig by a regulator. The air stream is passed through a scrubber system consisting of 4N NaOH to remove CO_2 and distilled water to saturate the air stream. A dead volume is placed before the 4N NaOH scrubber as a safety precaution in the event that the air system causes a backpressure forcing scrubbing solution against the air system. An empty impinger is placed after the water scrubber to separate larger water droplets from

Table 3-2. Properties of selected composts before and after incubation.

Property	Compost #1		Compost #2		Compost #3		Compost #6	
	Before	After	Before	After	Before	After	Before	After
	use	use	use	use	use	use	use	use
pH	8.67	6.79	8.13	8.44	9.22	8.72	7.26	7.55
Water (Wt%)	60.3	59.5	59.7	57.4	61.0	63.0	60.5	62.0
LOI (Wt%)	79.8	73.7	69.1	64.4	73.8	74.4	65.2	64.6
Water-P (mg/kg)	144	96.9	95.2	97.9	53.3	49.3	231	218
Total-C (Wt%)	36.9	39.6	36.8	35.3	39.5	40.9	39.5	36.2
Total-N (Wt%)	3.00	3.57	2.84	2.78	2.26	2.30	3.45	3.73
C/N	12.3	11.1	12.9	12.7	17.5	17.8	11.5	9.71
Metals (mg/kg)								
Ca	37400	40300	57500	60000	66500	65000	47700	49800
Mg	4120	4470	5250	5300	3840	4250	5400	5950
Zn	492	557	651	638	81.0	94.5	897	964
Cu	201	194	125	131	8.50	9.50	114	113
Mn	30.0	36.0	66.5	70.0	23.5	25.0	48.5	52.0
Fe	8820	9760	5220	5130	512	541	6740	7260

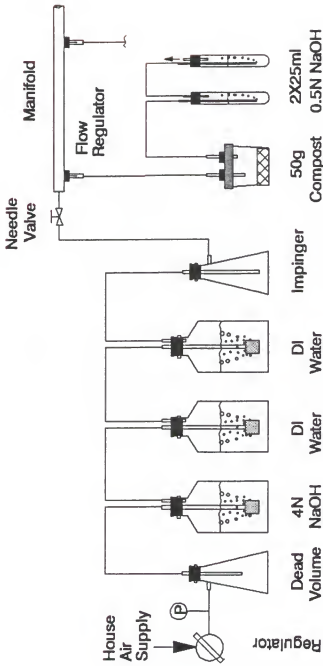


Figure 3-1. Schematic drawing of the experimental arrangement for the study of compost decomposition.

the air stream. Two water scrubbers are used in series to ensure that the air stream is completely free of alkali and to resaturate the air with water vapor in order to keep the water content of the composts constant.

The resaturated, CO_2 -free air stream is then forced to the manifold where it is split into 15 streams. Each stream goes into one incubation-absorption unit. Fifty grams of compost sample is put in each incubation bottle. The CO_2 evolved from each of the compost samples is collected in two 25-mL, 0.5N NaOH collectors in series. The total air flow rate is controlled by a needle valve located in front of the manifold. Syringe needles are used as flow regulators to equalize the air flow through the 15 incubation units. The air flow rate through each unit is adjusted to about 15 ± 2 mL/min. The incubation system is continuously operated at constant temperature ($23 \pm 2^\circ\text{C}$).

After flushing the residual air from the incubation bottles, the outlet tube of each bottle is attached to the CO_2 collectors. CO_2 collectors are replaced with fresh solutions periodically during the incubation period. The system is leak checked before the incubation. Evolved CO_2 is efficiently trapped by two absorption collectors in series. Tests have shown that the first tube absorbed more than 95% of the total CO_2 evolved.

CO_2 evolution is measured as described by Stotzky (1965) with minor modifications. After CO_2 absorption, the solutions in the two collectors of each unit are mixed and

titrated with standard 1N HCl. The CO₂ samples collected from each of the control bottles are concomitantly titrated.

The CO₂ evolved for individual samples is calculated as follows (Stotzky, 1965):

$$\text{CO}_2 = (B - V)NE \quad (\text{mg}) \quad (3-1)$$

where:

- B = volume of HCl used to titrate the NaOH in the controls to the end point, (mL);
- V = volume of HCl used to titrate the NaOH remaining in the CO₂ collectors after treatment to the end point, (mL);
- N = normality of the HCl, (meq/mL);
- E = equivalent weight, (mg/meq), for CO₂, E = 22 (mg/meq).

To investigate the effect of H₂S concentration on compost decomposition, one hundred grams of Compost #6 was used as the test material. The experimental arrangement for this test is similar to that for the compost decomposition test with some minor modifications (Figure 3-2). Room air is forced through a scrubber containing 4N NaOH to absorb CO₂ from the air stream. The CO₂ free air is then saturated by bubbling through DI water. Pure H₂S is then mixed with the pretreated air stream to obtain the test gas mixture with the desired H₂S concentration. The treated gas stream is vented through the manifold, where it is split into four sub-streams: one of these sub-streams is vented to a control column (empty), and the other three streams to duplicates of three compost columns. The gas is forced vertically through the compost from bottom to top at a flow rate of 30 mL/min.

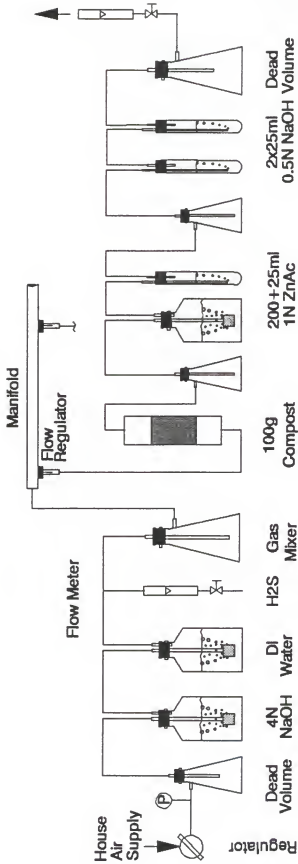
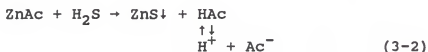


Figure 3-2. Schematic drawing of the experimental arrangement for the investigation of the effect of H_2S exposure on compost decomposition.

A portion of the hydrogen sulfide is adsorbed and/or oxidized by the compost and the remaining H_2S in the effluent gas is absorbed by two H_2S scrubbers in series which contain 200 mL and 25 mL 1N zinc acetate (ZnAc) solution, respectively. The absorbing reaction used by the H_2S collectors is:



Total flow in the system is measured by pre-calibrated rotameters. H_2S concentrations in the inlet gas to the compost column are controlled by adjusting the flow rates of mixing for the CO_2 -free air and the pure H_2S gas. Gas samples from the influent gas stream are taken periodically by gas-tight syringes, diluted with prepurified nitrogen (N_2) and analyzed for H_2S content by a Tracor 250H analyzer (See Chapter 4 for details). The effluent gas from the filter columns is first passed through two scrubbers in series containing 1N ZnAc to absorb any H_2S remaining in the gas stream. Residual CO_2 in the effluent gas stream is subsequently absorbed by 0.5N NaOH solution and titrated as described previously.

Each compost sample is incubated at a desired H_2S concentration level for 24 hours. After the incubation period the compost as well as the absorption solutions are replaced by fresh compost samples and absorbing solutions for operation at the next H_2S concentration level. The

system was previously tested to obtain absorption efficiencies of H_2S and CO_2 in the ZnAc traps. The results showed that the H_2S absorption efficiency was greater than 99% and the CO_2 absorption was less than 2% for the ZnAc solutions used.

Results and Discussion

Decomposition of Composts

The decomposed C evolved as CO_2 from the four composts studied during the 122 day incubation period is shown in Figure 3-3. The decomposition patterns of composts #2, #3 and #6 are somewhat similar. Decomposition of compost is initially rapid, from 40 to 52% of the total CO_2 produced in the 122 days is evolved in the first 42 days of incubation. A total of 9.2, 5.7, 6.1, and 4.4% of the original C was decomposed and released as CO_2 for composts #1, #2, #3, and #6, respectively during the total 122 days of incubation.

It appears that decomposition rates of the composts are inversely proportional to their age, in other words, the older the compost, the slower the decomposition. All except compost #1, showed decomposition rates which were similar. Compost #1, however, was not completely composted when used. Also the organic matter content of this compost is higher than that for the others tested. Initial and delayed higher decomposition rates for compost #1 suggest a two stage incubation involving an initial 'conditioning' step followed by a 'conditioned' decomposition. The compost

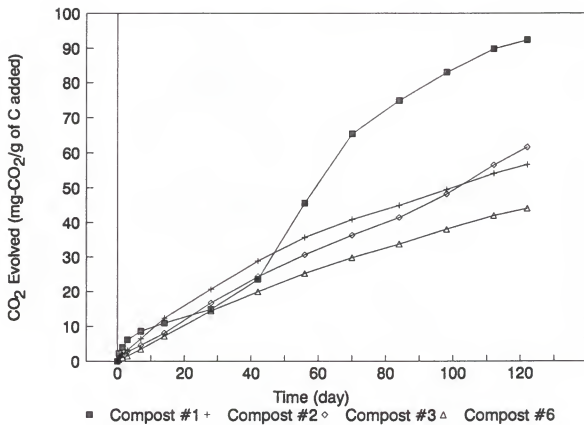


Figure 3-3. Plot of CO₂ evolution from composts during the 122 day incubation.

decomposition rates measured here are much slower than those found for soils. Tester et al. (1977) reported that approximately 16% of the compost C was evolved as CO_2 during 54 days of incubation, when 2 to 6% fresh sewage sludge compost was incubated with soils. Miller (1974) reported that 20% of added organic carbon is evolved as CO_2 for a 6 month incubation period under similar conditions. In another investigation carried out by Moorhead et al. (1987) it was observed that about 39 and 19% of the total-C for fresh and digested low-N plant biomass, and 50 and 23% of fresh and digested high-N plant biomass are released as CO_2 during 90 days decomposition when these biomasses are added to soils. Fresh plant biomass evolves as much as twice the organic-C as CO_2 when compared to corresponding digested biomass sludges. These results of other researchers suggest that the decomposition rate of organic matter strongly depends on the source and the properties of the available organic matter. Miller (1974), Sommers et al. (1976) and Terry et al. (1979a, b) have concluded that sludge composition and incubation conditions, rather than soil properties control sludge decomposition.

Reddy et al. (1980) have shown that decomposition of organic carbon depends on the nature and constitution of the wastes. Low molecular weight (simple) compounds can be more easily degraded by microorganisms than more complex organic compounds. Organic-C components in decreasing order of biodegradability are: (i) readily oxidizable soluble

organic-C, (ii) proteins, (iii) hemicellulose, (iv) cellulose, and (v) lignin. In the examples mentioned above, fresh plant biomass releases much more CO₂ (especially in the early stages of the incubation) than the digested ones because it contains much more easily decomposable organic-C. In this study, all the composts used were well aged or completely composted. Most of the easily decomposable organic-C such as soluble organic-C, starch and proteins have been decomposed during the composting process. The main organic-C species remaining in the composts studied are the more oxidation resistant residues of the original organic matter (Biddlestone et al., 1987). Also, the four composts studied are either yard waste compost or mixtures of sewage sludge with yard wastes such as wood chips, leaves and tree trimmings, etc.. A high content of cellulose and lignin can be expected in these materials. This feature may explain why the decomposition rates for the composts studied here are relatively low.

Decomposition of a complex substrate C is usually described by a multistage first-order decomposition sequence (Reddy et al., 1980; Gilmour et al., 1985). The mathematical rate equations can be written as follows:

$$-dC_i/dt = k_i C_i \quad (3-3)$$

where *i* refers to a particular stage of decomposition.

The integrated form of equation 3-3 becomes:

$$C_{ti} = C_i \exp(-k_i t) \quad (3-4)$$

where:

C_i = organic-C present at the beginning of a decomposition stage.

C_{ti} = organic-C present at the end of a decomposition stage at time = t , and

k_i = the first-order reaction rate coefficient.

Decomposition stages and the corresponding reaction rate coefficients for the four composts are presented graphically in Figure 3-4. The decomposition of compost #3 is described in one stage and the decompositions of compost #2 and #6 are best described in two stages. It can be seen that the reaction rate coefficient values of k_1 and k_2 for these two composts are very similar. This similarity indicates that these two composts have similar organic C composition.

The behavior of Compost #1 is markedly different from those of the other composts. During the first 3 days of incubation, CO_2 evolution is rapid followed by a lag period, lasting for the following 40 days. A second period of high decomposition rate was observed between 42 and 70 days. During the remaining period of incubation (after 70 days), the CO_2 evolution rate for this compost is similar to those for the other composts. The decomposition rate for compost #1 may be described as a 3 stage series of first-order reactions.

Within overall experimental error, reaction rate coefficients for the final stage of decomposition for the

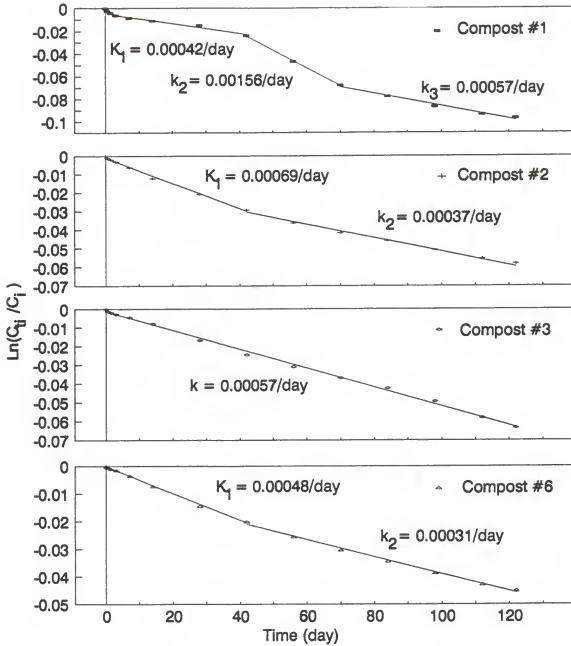


Figure 3-4. Decomposition stages and reaction rate coefficients for the four composts studied.

four composts studied are quite similar, falling in the range from 3.1×10^{-4} to 5.7×10^{-4} /day. If the second reaction rate coefficients for the composts studied can be assumed to be representative through the remaining life of the compost, then a rough estimate of the time required for decomposition of 50% of the organic matter (half life) in these composts can be made according to following equation.

$$t_{0.5} = 0.693/k \quad (3-5)$$

where:

$t_{0.5}$ = the half life time of the compost, (day), and
 k = the first-order reaction coefficient, (1/day)

The estimated half life time of the composts tested is from 3.3 to 6.1 years. This estimate is comparable to the result reported by Varanka et al. (1976), who showed that it takes approximately 6 years to lose 50% of the sludge organic C when used in the field.

No significant changes in other physical and chemical properties of the composts were observed for the 120 day incubation period used in these studies (Table 3-2).

Effect of H_2S on Compost Decomposition

The effect of H_2S exposure on compost decomposition is illustrated in Figure 3-5, where CO_2 evolved by the composts is expressed as mg- CO_2 per g-C of the compost as a function of the H_2S concentration (ppmv). The CO_2 evolution is significantly increased with the increasing H_2S concentration. The rate of this increase is greater at

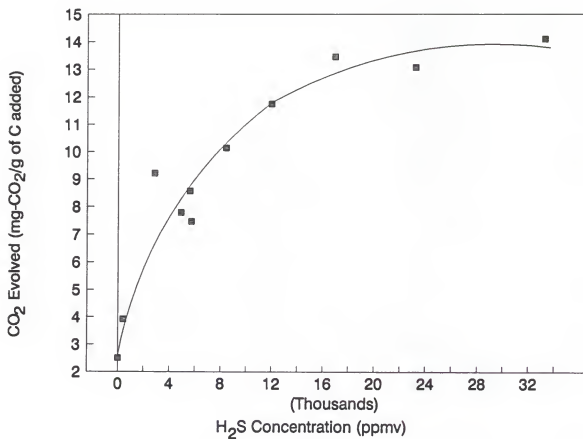


Figure 3-5. Effect of H_2S exposure on the rate of compost decomposition as measured by CO_2 respiration.

lower H_2S concentrations. For example, the CO_2 evolved at H_2S concentrations near 6,000 ppm is approximately 8.5 mg- CO_2 /g-C added, which is about 3.4 times that evolved when no H_2S is present. At higher H_2S concentrations the increase of CO_2 evolution with H_2S concentration is reduced e.g. when the H_2S concentration is increased from 12,000 ppm to 32,000 ppm the CO_2 evolution increases only by about 17%, or approximately 2 mg- CO_2 / g-organic matter.

It can be seen from Figure 3-5 that the CO_2 evolution from the compost has a strong dependence on the H_2S concentration in the gas to which the compost is exposed. A linear relationship is obtained when plotting CO_2 evolved as a function of the square root of H_2S concentration in the gas, $[\text{H}_2\text{S}]^{0.5}$ for the range of H_2S concentration less than 17,000 ppmv (Figure 3-6). The regression analysis result for the best fit line is:

$$\text{CO}_2 = 2.62 + 0.082[\text{H}_2\text{S}]^{0.5} \quad (3-6)$$

where:

$$\begin{aligned} \text{CO}_2 &= \text{CO}_2 \text{ evolved from compost, (mg/g of C added)} \\ [\text{H}_2\text{S}] &= \text{H}_2\text{S concentration in the inlet gas stream,} \\ &\quad (\text{ppmv}) \end{aligned}$$

The correlation coefficient, R^2 for the variables is 0.9234.

Equation 3-6 quantitatively describes the effect of H_2S on the decomposition of composts. For example, CO_2 evolutions at $[\text{H}_2\text{S}] = 0$ and $[\text{H}_2\text{S}] = 1000$ ppmv are calculated

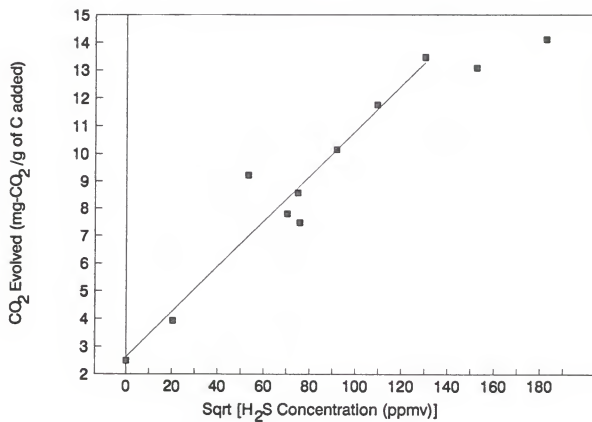


Figure 3-6. Plot of CO₂ evolution as a function of square root of H₂S concentration.

to be 2.62 and 5.21 mg-CO₂/g-OM, respectively, by equation 3-6. The ratio of these two values is equal to the ratio of the first-order reaction coefficients for the reactions at these two conditions,

$$\text{CO}_{2,1000}/\text{CO}_{2,0} = k_{1000}/k_0 = 1.99.$$

in other words, the decomposition rate for the compost exposed to 1000 ppmv H₂S is 1.99 times of that for the compost not exposed to H₂S. The half life times for compost #6 at both conditions are:

$$t_{0.5,0} = 0.693/0.00031 = 6.12 \text{ (years)}, \text{ and}$$

$$t_{0.5,1000} = 6.12/1.99 = 3.08 \text{ (years)}.$$

and for compost #3 are:

$$t_{0.5,0} = 0.693/0.00057 = 3.33 \text{ (years)}, \text{ and}$$

$$t_{0.5,1000} = 3.33/1.99 = 1.67 \text{ (years)}.$$

No studies of similar effects have been reported in the existing literature. Thus the results obtained in this study can not be compared with the results of other investigations. Taylor et al.(1978) found that the highest S mineralization rates are observed during the period of highest CO₂ evolution when 2 to 6% of sewage sludge compost is incubated in soils. Their results and those reported here suggest that the microbial activity of the compost was significantly enhanced by the addition of H₂S, especially the activity of the sulfur oxidizing bacteria.

Oxidation of inorganic sulfur compounds is a basic phenomenon in nature. A number of bacteria have been

identified in soils and other environments that are capable of oxidizing organic and inorganic sulfur compounds (Roy and Trudinger, 1970). A high population of the oxidizing bacteria can be expected in the composts tested here. With sufficient H_2S supply, the bioactivity of the sulfur oxidizing bacteria can be stimulated to result in an increase of microbial population and a corresponding increase in the evolution of CO_2 . Hydrogen sulfide is finally oxidized to sulfate through various pathways and intermediate stages (Roy and Trudinger, 1970; Brock and Madigan, 1988; Yang and Allen, 1991; Allen and Yang, 1991).

After the 24 hours reaction period, the color of the compost changed from originally brown to yellowish-white, especially at high H_2S concentrations. This feature indicates that a large amount of sulfur has accumulated in the compost.

Conclusions

Among the various biofilter materials, compost is frequently selected as a medium in applying biofiltration to air pollution control due to its unique properties and advantages. Knowledge of the characteristics of compost decomposition are important for both prediction of biofilter operation characteristics and degradation estimates, as well as in deciding on the appropriate disposal treatment and method for used compost. The studies described here indicate that the decomposition rates of the composts tested are much

lower than those reported by other researchers, who used fresh composts mixed with soils. Five to ten percent of the total-C in composts were decomposed during the 122 days incubation period. Compost half life times of the order 3 to 6 years are estimated for the composts studied, corresponding to loss 50% of their total-C due to decomposition. A multi-stage first-order reaction sequences is used to describe the decompositions. First-order reaction rate coefficients have been determined.

Decomposition rates are significantly increased when H_2S is introduced to the compost. The half life of the compost is significantly reduced as a result of increased biological activity and CO_2 respiration. For example, continuous exposure of compost to 1000 ppm H_2S can result in reduction of the half life of the compost from about 6 years to 3 years due to enhanced microbiological activity alone. The results suggest that added H_2S was oxidized by the sulfur oxidizing bacteria in the compost to sulfate.

CHAPTER 4
DETERMINATION OF THE DESIGN AND
OPERATIONAL PARAMETERS FOR BIOFILTER SYSTEMS

Introduction

Extensive experimental work has been carried out in order to determine the design and operational parameters for a biofilter system. This research is essential for best operation as an air pollution control technology and for optimization of the system. This chapter describes the design and construction of lab scale biofilter systems, experimental methodology used and the results obtained.

System Design and Construction

Three biofilter systems were designed and constructed for different investigative purposes. Each system can be operated and controlled separately. Detailed information on each experimental system is presented below.

The Dual Tower System

Most of the experimental work was carried out using a dual-tower experimental biofilter system. This configuration, which is shown in Figure 4-1, consists of parallel dual column filters. The two biofilter columns, identified as Tower #1 and Tower #2, can be run

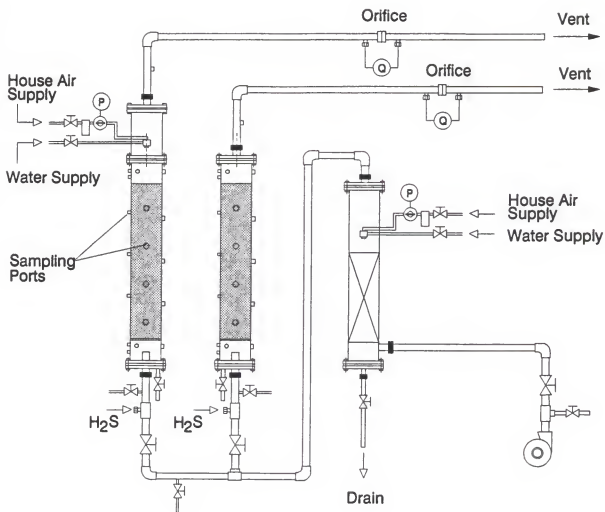


Figure 4-1. Schematic drawing of the dual tower system.

simultaneously and controlled separately. The biofilter bed material is enclosed in transparent rigid Acrylic pipe, with an inner diameter of 0.15 meters (6 inches) and a height of 1.34 meters (4 feet). Each vertically mounted pipe can be packed with the desired compost up to a height of 1.2 meters (3.9 feet). The packed biofilter material is supported by a sieve plate to ensure a homogeneous distribution of the inlet gas stream across the face of the bed. Non-biodegradable plastic screens are placed between the sieve plate and the biofilter material to avoid separation of smaller compost particles.

Sampling and measurement ports are located along the Acrylic column for compost and gas sampling, and pressure and temperature measurements. The sampling and measurement ports are shown in Figure 4-2a and b for Towers #1 and #2, respectively. An individual sampling/measurement port is identified by a letter-number system, where the letter indicates the function and the number indicates the location of the port. For example, TS11 means this port is used for temperature measurement and solid sampling, and is located on Tower #1 at location 1. All the other filter systems with multi measurement/sampling ports are identified in the same manner.

Room air is forced by a Gast Regenair Model R3105-1 air blower into the humidification chamber. The blower, which is driven by a 1/2 HP motor, generates a maximum flow of $1.5 \text{ m}^3/\text{min}$ (53 cfm) and a maximum pressure/vacuum of

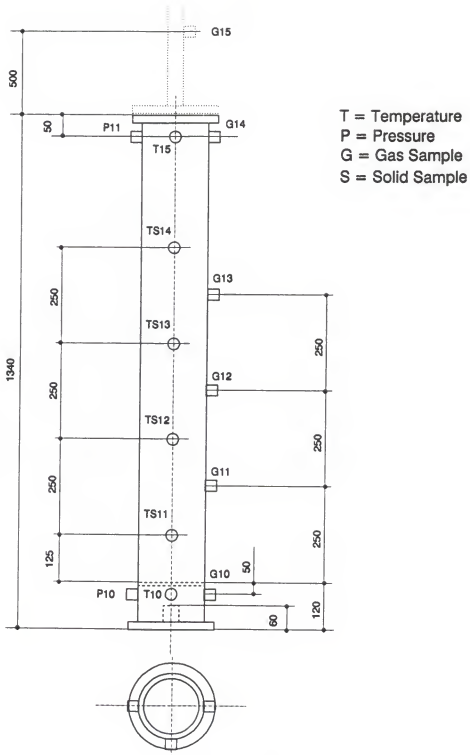


Figure 4-2. Sampling and measurement ports on towers.
 a. Tower #1

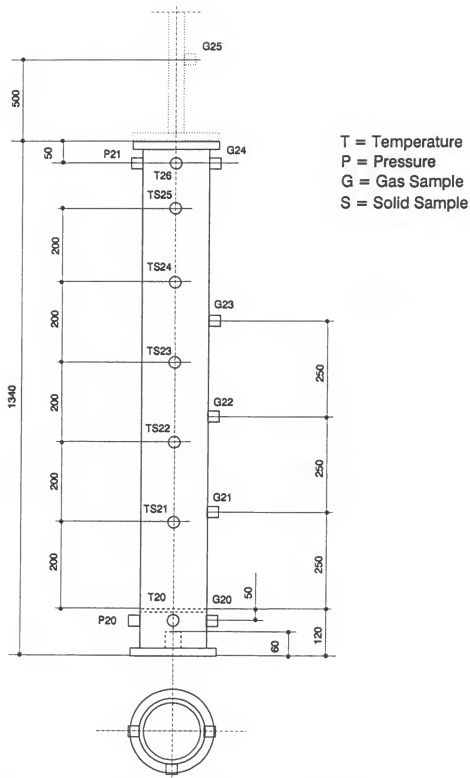


Figure 4-2. Sampling and measurement ports on towers.
 b. Tower #2

1100/1000 mmH₂O (43/40 inches) of water column. Humidification of the inlet air is achieved by atomizing water in the spray chamber, through which the room air passes. In addition, Pall rings are stacked in the spray chamber for extending wetted surface area providing better humidification. As a result relative humidities in the range 95 to 100% were routinely and continuously achieved.

Gaseous H₂S with a purity of 99+%, which is stored in liquid form under pressure in a cylinder, is continuously leaked and mixed with the prehumidified air in the inlet lines (PVC pipe) to the towers. Plastic screen packing is placed downstream from the H₂S introduction point for better mixing. Flow rates of air and H₂S are controlled by plastic valves, which are located on the carrier gas inlet lines, and stainless steel needle valves, respectively. The flow rates are measured on calibrated flow meters to obtain the desired H₂S concentration and gas flow through the towers. Measurements of temperature, pressure and gas flow rate are discussed in later sections.

A nozzle is installed on the top of Tower #1 in order to introduce water, or other liquid solutions if necessary, to the outlet end of the bed. Gas lines are made from PVC pipes. The towers and pipes are connected by flanges for convenient dismantling of the packed towers and compost changes. Cork-rubber gaskets are used to seal the flanges.

Portable Tower #3

The portable tower is made from PVC pipe with an inner diameter of 77 mm (3 in). This tower, which is shown in Figure 4-3, has a total height of 1.2 meters (3.94 ft) with an effective packing height of 1 meter (3.28 ft). The two ends of the pipe are covered by rubber caps and held by pipe clamps. Compost packed in the tower is supported by a packing of non-biodegradable plastic screen. Measurement ports for pressure, temperature and exhaust gas samples are located along the length of the tower. Gas to be tested is introduced through a port at the bottom of the tower. The overall gas flow rate is measured by a pre-calibrated flow meter after the effluent gas passes through a particulate filter. This portable tower was used intensively for pressure drop studies and for investigation of long term operation of compost #16.

Column System #4

A fourth column biofilter system was constructed for investigation of the effects of various operational variables on H_2S removal (Figure 4-4). This multicolumn system includes eight compost columns, a manifold for introduction of test gas and several needle valves for flow control. The columns are made from PVC pipes with an inside diameter (ID) of 35 mm (1.25 in). Each column has a length of 300 mm (12 in) and an effective packing height of 250 mm

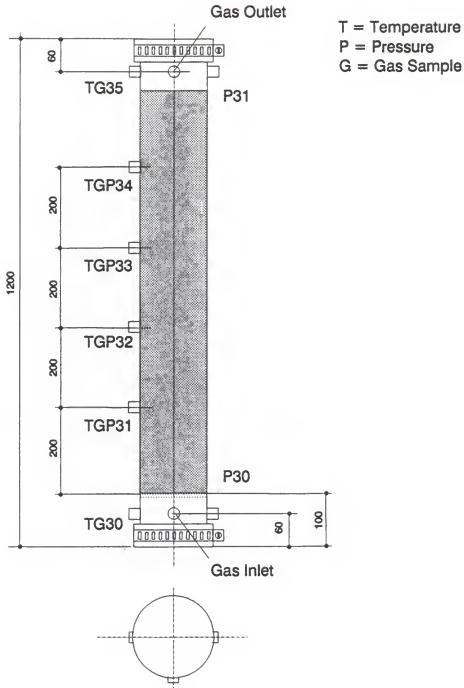


Figure 4-3. Schematic drawing of Tower #3.

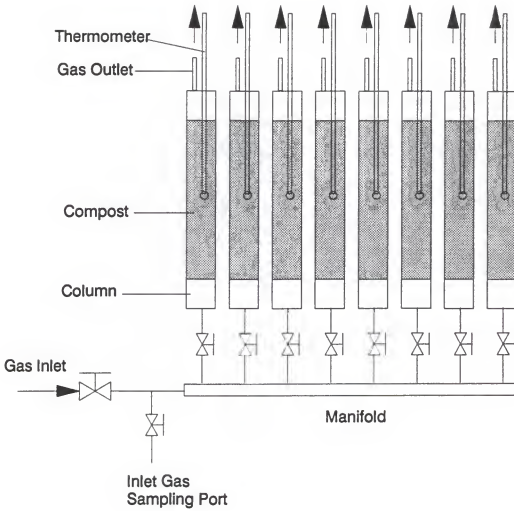


Figure 4-4. Schematic drawing of column system #4.

(10 in), which provide a 240 mL packing volume. The ends of the packed columns are plugged by rubber stoppers. Thermometers are inserted into the columns to measure temperatures. The gas flow rates are measured by a rotameter at the gas outlets. Effluent gas samples are taken from the outlet of the rotameter.

Measurement Methods

Periodic measurement of temperature, pressure drop and gas flow rate in the biofilter systems are carried out by the following devices.

Temperature

Temperature is measured by mercury in glass thermometers with a range from -20°C to 110°C and a minimum scale division of 1°C .

Pressure Drop

Pressure drop is measured by manometers with a minimum reading of 1 millimeter water column (mmH_2O). In case the pressure drop is greater than $1000 \text{ mmH}_2\text{O}$, the pressure drop is measured by mercury manometers with a minimum reading of 1 millimeter of mercury (mmHg).

Gas Flow Rate

All the gas flow rates except those of Towers #1 and #2 are measured by pre-calibrated rotameters.

The gas flow rates in Towers #1 and #2 are measured by specially designed orifices. Two orifices for each tower were designed and made, one for low flow ranges and the other for high flow ranges. The orifices are made from plastic plate and installed on the outlet gas pipe lines (see Figure 4-1). The pressure drops across the orifices are measured and the flow rates are calculated according to the developed calibration equations.

Sampling Methods

Compost Samples

Compost samples in Towers #1 and #2 are taken from the solid sampling ports shown in Figures 4-2 a and b. The samples are taken at each port in a radial direction to the tower walls so that a representative sample can be obtained for that section. For composts not initially packed in columns, the samples are taken after the compost has been thoroughly mixed and very large particles (diameter > 10 mm) have been eliminated.

Gas Samples

The inlet and outlet gas samples for each system are obtained directly from the gas sampling ports by extraction using gas-tight syringes. Gas samples extracted from other locations along the towers are obtained by using a gas sampling probe assembly. The gas sampling assembly, as

shown in Figure 4-5, consists of a Teflon probe, a Teflon filter and a sampling port connector. The Teflon probe is made from a piece of Teflon tubing (6.35 mm (1/4") in diameter), with 14 holes (1mm diameter) spaced evenly along the probe length. The probe is installed in the towers in such a way that all the holes are perpendicular to the tower's normal axis. Thus, representative gas samples from a cross section of the tower can be obtained. The Teflon filter is used to block out any small particles and water droplets which may be extracted during sampling. Gas samples are obtained through the sampling port located on the end of the assembly (see Figure 4-5) by a gas-tight syringe. The sampling port is sealed by a rubber GC septum.

When taking a sample, at least three full syringes of gas sample are wasted before the actual sample is taken for analysis. This procedure will eliminate residuals of previous gas samples remaining in the Teflon filter holder, in the syringes and in the probe, as well as condition the extraction system to the gas being sampled.

The gas samples are then diluted in 3-L Tedlar sampling bags by pure nitrogen (N_2) to an appropriate concentration within the calibration range of the analyzer. The gases in the Tedlar bags are thoroughly mixed by gently kneading the bags and allowing them to sit for at least 10 minutes before analysis. Most of the samples taken are analyzed within 2 hours.

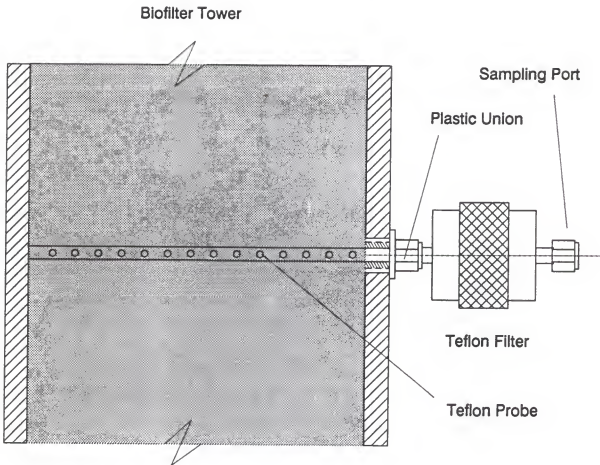


Figure 4-5. Schematic drawing of the gas sampling assembly.

In most cases, the H_2S concentrations in the outlet gases are so low that the gas samples can be analyzed directly without any dilution. In the latter cases, Tedlar bags are directly connected to the sampling ports. Gas samples are forced into the bags as a result of the positive pressure of gas within the tower system. Also, Teflon filters are replaced by glass wool plugs to reduce the resistance to flow.

Each time after use, the Tedlar bags are purged at least three times with N_2 to eliminate residual gas and vapor. The stability of gas samples in the Tedlar bags are discussed in Chapter 6.

Water Samples

Water samples analyzed are mainly biofilter wash waters from the tower drain outlets. When washing a packed tower, the entire wash water is collected in a container. Water samples are obtained from the container after mixing the wash water with a stirrer for a few minutes.

Compost Analysis Methods

Water Content

Two to five grams of wet compost are dried in an aluminum tray at an oven temperature of $70^\circ C$ until constant weight is obtained. Compost water content is determined by the difference in weight between the wet and dry composts (Robarge and Fernandez, 1986).

pH

A known amount of wet compost is weighed into a 50-mL container. DI water is added to bring the liquid/solid ratio to 10 (Robarge and Fernandez, 1986). The sample is shaken for 30 minutes by a rotary shaker. Measurements of pH are made by a calibrated Corning Model M245 pH meter, which is accurate to ± 0.01 pH.

Total Carbon and Total Nitrogen

Finely-ground, oven-dried compost sample (<100 mesh) are analyzed for total carbon and total nitrogen using a Carlo Erba Model NA 1500 CNS Analyzer.

Water Soluble Phosphorus (WSP)

A known amount of wet compost (2.5 g dry weight equivalent) is weighed into 50-mL centrifuge tubes. DI water is added to the tubes to obtain a compost to liquid ratio of 1:10 on a dry weight basis. These samples are allowed to agitate for a period of one hour on a mechanical shaker. The compost suspensions are then centrifuged at 6000 rpm for 15 minutes and filtered through Gelman 0.45 micrometer membrane filters. The filtered solutions are acidified ($\text{pH} < 2.0$) with one drop of concentrated H_2SO_4 and stored at 4°C until analyzed. The soluble reactive P (SRP) in the filtered extract is determined colorimetrically (APHA, 1989) using a Shimadzu UV-160 spectrophotometer with 1 cm path length at 880 nm wavelength.

Acid-extractable Cations

Two and half (2.5) g of finely-ground, oven-dried sample is weighed into 50-mL centrifuge tubes. Twenty five (25) mL of 1M HCl is added and the tubes are shaken for 3 hours on a mechanical shaker. The compost suspensions are centrifuged at 6000 rpm for 15 minutes and filtered through Gelman 0.45 micrometer membrane filters. The solutions are analyzed for Fe, Al, Ca, Mg, Cu and Mn on an Inductively Coupled Argon Plasma Spectrometer (ICAP) (APHA, 1989).

Particle Size Distribution

The compost is dried in oven at 70°C for 24 hours. Particle size distribution by weight is measured by passing the dried compost through a series of sieves (U.S.A. Standard Testing Sieve, A.S.T.M. E-11 Specification, Fisher Scientific Company) and weighing the residue.

Porosity

Compost porosity is determined according to Danielson and Sutherland (1986).

Organic Matter

After determination of compost water content, the samples are placed in a muffle furnace and baked for 24 hours at 450 °C. Organic matter is determined by the loss-on-ignition (LOI) (Robarge and Fernandez, 1986).

Particle Density

Particle density of the compost is measured according to Blake and Hartge (1986a).

Bulk Density

Bulk density of the compost is measured according to Blake and Hartge (1986b).

Sulfur Analysis Methods

Intensive and detailed laboratory work has been carried out on the analysis of sulfur compounds in order to obtain a better understanding of the biochemical reactions involved in the H_2S oxidizing processes occurring in the biofilters. The procedures for determining various sulfur compounds in compost, in water, and in the waste gases are described in this section.

Sulfur in Compost

The analysis of sulfur in compost includes the determination of total sulfur (total-S) and fractionation of the total sulfur into inorganic and organic constituents.

Many wet chemical procedures have been developed to fractionate the total sulfur pool in sediments, soils, and peat into its inorganic and organic constituent compounds. Very little information, however, is available about such analyses for compost. The sulfur analyses conducted in this research include the quantitative determination of acid

volatile sulfur (sulfide-S), water soluble sulfur (soluble sulfate), insoluble sulfate (SO_4^{2-}), elemental sulfur (S^0), Pyrite sulfur, ester sulfur (organic-S) and total sulfur.

Each of the wet chemical procedures involved the reduction of S to H_2S in a Johnson-Nishita apparatus (Johnson and Nishita, 1952) and trapping the evolved H_2S in zinc acetate-sodium acetate (ZnAc-NaAc) solutions. Trapped sulfide is quantified by iodometric titration (APHA, 1989) with a 0.025N iodine solution and 0.025N $\text{Na}_2\text{S}_2\text{O}_3$ titrant.

The distillation apparatus incorporated slight modifications of that used by Johnson and Nishita and is similar to that used by Wieder and Lang (1985). Figure 4-6 shows the distillation assembly. The reaction flask is a 250-mL, round-bottom, three-neck flask, with an N_2 inlet via a bleed tube inserted in one neck and the central neck is connected to a condenser. Ultra high purity (>99.999%) nitrogen is used to sweep out the H_2S and to maintain the reaction flask in a reducing environment. The third neck of the flask is fitted with a stopper to allow introduction of liquid solutions to the flask. The ZnAc-NaAc solution is made by dissolving 50 g of zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and 12.5 g of sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) in 800 mL of DI water and adjusting the final volume to 1 liter (Tabatabai, 1982). Twenty-five (25) mL of this solution is mixed with 100 mL of DI water and this solution is used to fill two traps used in series. The first trap contains 100 mL and the second one contains 25 mL



Figure 4-6. Photograph of the sulfur distillation assembly.

of the H_2S absorption solution. Even though the contents of both traps are analyzed, more than 95% of the H_2S is consistently recovered in the first of the two series traps. The material to be analyzed is added to the reaction flask through the side neck. The system is purged with N_2 at bubbling rate of 1-2 bubbles per second in the ZnAc-NaAc traps for 10 minutes before the introduction of additional reagents. The materials are boiled for 1 hour, the traps are removed and sulfide titrated.

The procedures and methods used for analysis of the total sulfur and various organic and inorganic sulfur compounds in compost are similar to those used for sulfur analyses in peat, soil and sediments described by Zhabina and Volkov (1978), Tabatabai (1982), and Wieder and Lang (1985). Minor modifications were made for the compost sulfur analyses in this research. The procedures are illustrated in Figure 4-7.

All results are expressed as mg sulfur per gram of compost on a dry basis (mg-S/g). Compost moisture content is determined from a sub-sample by drying the compost at 70°C to constant weight.

Compost samples are stored in plastic bottles and refrigerated at $2-4^\circ\text{C}$ before analysis. In most cases, however, compost samples are analyzed immediately after sampling.

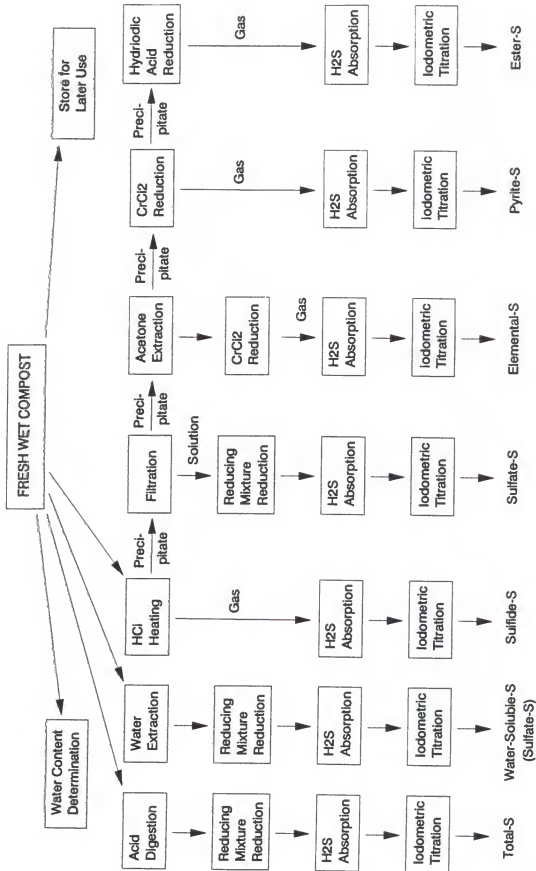


Figure 4-7. Flow chart of the sulfur analysis procedures for compost.

The fresh wet compost sample is divided into five sub-samples. The latter are used for the analyses of 1) compost moisture content, 2) total-S, 3) water-soluble-S, 4) inorganic and organic sulfur fractions, and 5) storage for later use.

Total sulfur

Total-S is determined by oxidation (acid digestion) of the various reduced sulfur constituents to sulfate and followed by reduction of the sulfate to H_2S . The H_2S is then trapped and titrated as described above. In most of the analyses, 0.5-5.0 g of fresh compost is used, depending on the sulfur content. In some analyses, oven dried compost is used. In the latter case, the compost samples are finely grounded (<40 mesh) and a correspondingly smaller size of compost sample is used. The compost is subjected to acid digestion as described by Tabatabai (1982). The digest is quantitatively transferred into a 100-mL volumetric flask and the volume is adjusted with 1N HCl. Reduction of the sulfate is carried out by a reducing mixture. The reducing mixture contains 50% hypophosphorous acid, 90% formic acid, and hydriodic acid in a 4:2:1 proportion and is prepared as described by Tabatabai (1982). Depending on the sulfur content, 1 to 5 mL aliquot of the digest is transferred into the distillation flask. With aliquots >2 mL, the volume is reduced to about 2 mL by heating the flask on an electric heating mantle. Five (5) mL of the reducing mixture is

added to the flask and the material is subjected to reduction and hydrogen sulfide is liberated, collected and titrated as described above.

Water soluble sulfur

Water-soluble-S is determined by shaking 2-5 g of fresh compost in DI water with a liquid to solid ratio of 10:1 for 30 minutes on a rotary shaker at a speed of 140 /min. An aliquot of the compost extract is then subjected to reduction, H_2S absorption, and titration successively, as described previously.

The following analyses are conducted in succession:

Sulfide sulfur

Sulfide-S or acid-volatile sulfur (AVS) is determined by introducing 8 mL of 12N HCl to the compost sample in the reaction flask. Heat is applied after 10 min, the materials are brought to boiling, and after 45 min the traps are removed and the sulfide titrated.

Sulfate sulfur

The content of the reaction flask is filtered by a #42 Whatman filter. The filtrate is then subjected to reduction. H_2S is then trapped and titrated. This is an alternative way of carrying out sulfate analysis. The results are comparable to the summation of water soluble-S and P-extractable-S.

Elemental sulfur

The precipitate obtained above is dried with filter papers as described by Zhabina and Volkov (1978) and is extracted with analytical grade acetone. The volume of acetone used (mL) is 40 times that of the equivalent dry weight of the compost sample (g). The extraction flask is covered with Parafilm and placed on a rotary shaker at a speed of 140/min for 16 hours. The mixture is filtered and rinsed with additional acetone. Either a fraction of or the entire filtrate are subjected to Cr^{2+} reduction as described by Zhabina and Volkov (1978).

Pyrite sulfur

The residue left after S^0 extraction is subjected to chromium reduction. The Cr^{2+} was produced by passing a 1 M solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.5 M HCl through a Jones reductor column containing Zn amalgamated with Hg (Zhabina and Volkov, 1978). Preparation of the Jones reductor is described by Swift (1950) and Patterson and Thomas (1952). Ten (10) mL of ethanol is added to the flask followed by 20 mL of 12N HCl and 16 mL of 1M CrCl_2 solution. Heat is applied after 30 min, the H_2S evolved is absorbed in the traps and titrated as above.

Organic sulfur

Following the previous procedure, the insoluble residue in the reaction flask is filtered through a #42 Whatman filter and is washed repeatedly with acidified DI water to remove chromium ions. The residue is then subjected to reduction with the reducing mixture as described above. The organic sulfur determined this way is mainly ester-S.

In addition to the literature mentioned above, similar and dissimilar procedures for determining sulfur constituents in sediments, peat and soil are also described by Smittenberg et al. (1951), Freney (1958) , Johnson and Henderson (1979), David et al. (1982), and Hsieh and Yang (1989). An excellent comparison of some of these methods is reported by Wieder and Lang (1985).

Sulfur in the Aqueous Phase

Sulfur in water samples, such as in tower wash water and drainage, are analyzed for sulfide, sulfate, and/or total sulfur.

Sulfate sulfur

Sulfate in most of the water samples is determined by a turbidimetric method (APHA, 1989). A Milton Roy Model Spectronic 21 Spectrometer was used at 420 nm to measure the turbidity. Color or suspended matter in large amounts will interfere with this method. In the case of dark colored

water samples, the reduction, H_2S absorption and iodometric titration procedures described previously are used.

Sulfide sulfur

Sulfide was measured according to APHA (1989). The samples are pretreated to remove interfering substances and to separate insoluble sulfide.

Total-S

Total-S was determined by using 2-5 mL of the aqueous sample depends on its sulfur content. The sample is then analyzed as described for the total sulfur in compost.

Sulfur in Waste Gas

Gas samples are analyzed by a commercial gas chromatograph equipped with a flame photometric detector (GC/FPD), a Tracor Model 250H Analyzer. The detection limits and operational conditions for the analyzer are summarized in Table 4-1. Detailed information concerning the principles and conditions of operation are reported elsewhere (Yang, 1988). In the early stages of this study, the component peaks are recorded by a chart recorder (Texas Instruments, Inc., Model Recti/Riter II) and concentrations of sulfur compounds are determined by measuring the peak heights. Later in the study (from August 1990 to September 1991) the chart recorder was replaced by a Spectra-Physics model SP4290 integrator and the measured concentrations are read

Table 4-1. Retention times, limits of detection and operating conditions for the Tracor 250H Analyzer.

Item	Compounds ^a		
	H ₂ S	MM	DMS
Retention Time (min)	1.15	2.16	4.02
Detection Limit (ppmv)	0.01	0.01	0.02

Operating Conditions:

Temperatures: Valve: 50 °C
 Column: 70 °C
 Detector: 110 °C

Flow Rates: Nitrogen: 80 mL/min (carrier gas)
 Oxygen: 21 mL/min (flame gas)
 Hydrogen: 80 mL/min (flame gas)
 Sample: 40 mL/min

Cylinder Pressures: Air 40 psig (for sampling valve activation)
 Hydrogen: 53 psig
 Oxygen: 40 psig
 Nitrogen: 80 psig

^a MM: methyl mercaptan.
 DMS: dimethyl sulfide.

directly from the printout of the integrator. The Tracor analyzer is periodically calibrated for H_2S , methyl mercaptan (MM) and dimethyl sulfide (DMS) with standards purchased from National Speciality Gases, Inc.

Results and Discussion

Biofiltration is a process that involves physical, chemical, and biological processes. Many variables, such as temperature, compost water content, specific acidity of compost, sulfate content in the compost etc., can affect the function of the system. It is impossible to obtain optimum, longer term performance from a biofiltration system without an in depth understanding of the system properties and proper control of important variables. Extensive evaluations of the system properties have been conducted during the course of this study. The results presented in this section are divided into several subsections according to specific investigations undertaken. Composts from different sources (Table 3-1) have been used in the laboratory studies. The physical and chemical properties of these composts are summarized in Table 4-2. Applications of each of these composts are mentioned in the corresponding study subsections.

Pressure Drop

The energy consumption obtained in operating a biofiltration system is primarily that required by the

Table 4-2. Summary of initial compost properties.

Property	Compost ID #				
	12	13	14	16	17
pH	2.61	1.60	6.44	6.66	8.10
Bulk Density (g/cc)	0.30	0.27	0.18	0.22	0.20
Particle Den. (g/cc)	--	1.73	1.75	1.90	1.78
Porosity (%)	--	84.3	89.7	88.4	88.7
Water Content (wt%)	45.6	54.9	62.4	56.5	62.7
Organic Matter (wt%)	66.5	66.8	59.3	64.3	62.6
Total-S (mg-S/g)	44.8	70.4	--	--	0.74
Water-P (mg/kg)	140	223	152	114	167
Total-C (wt%)	34.3	31.0	31.3	30.5	40.9
Total-N (wt%)	1.89	3.24	1.75	4.27	1.30
C/N	18.1	9.57	17.9	7.14	31.5
Metals (mg/kg)					
Ca	47400	28900	145000	18000	26700
Mg	280	255	4880	1450	120
Zn	38.0	48.0	201	66.5	18.0
Cu	121	91.0	60.0	11.0	93.5
Mn	5.50	55.0	96.5	89.5	9.50
Fe	1900	805	6160	529	1510

blower (fans) to move contaminated air at the specified flow rate through the filter bed. However, the pressure drop across the filter bed increases markedly as the flow rate is increased. Since the pressure drop will be determined by the depth of the filter bed it is necessary that the gas velocity should be kept as low as possible.

The pressure drop across a compost bed filter can be lowered by physical treatment of the compost particle content. Such a procedure is an important requirement in optimizing the operation of a filter bed, because operation at a reduced resistance to flow allows the gas velocity as well as the volumetric flow rate to be significantly increased with little or no change in energy consumption. This will in turn increase the biofilter capacity and reduce the required filter size.

The following physical factors determine pressure drop across the filter bed:

- 1) Particle size distribution in the compost
- 2) Condition of the filter packing
- 3) Height of the filter bed
- 4) Water content of the compost
- 5) Gas velocity, and
- 6) Porosity of the compost.

A representative sample of compost #12 was air dried and the particle size distribution determined by weighing the fractions penetrating a series of standard sieves. The particles are classified into 5 size groups in the range >12 mm to <1.2 mm (see Table 4-3). Compost samples in each of

Table 4-3. Particle size range distributions for selected composts.

Compost ID #	Particle Size Range Distribution (wt%)				
	A	B	C	D	E
12	20.0	22.5	10.0	13.1	34.4
14	27.7	26.9	8.10	11.6	25.7
13	21.4	24.5	6.70	15.8	31.6
17	0.00	33.4	14.4	22.5	29.7

A: diam. > 12 mm

B: 3.35 < diam. <12 mm

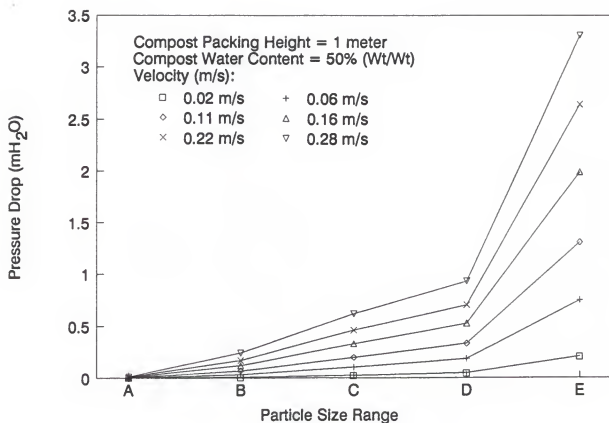
C: 2.36 < diam. <3.35 mm

D: 1.18 < diam. <2.36 mm

E: diam. <1.18 mm

the particle size groups were analyzed for water content then wetted to obtain a water content of about 50%, by spraying and mixing water with the compost samples. These treated samples were then used to determine the pressure drop as a function of the 5 particle size range classes by adjusting air velocities in the range 0.02 m/s to 0.28 m/s. All tests were carried out with the same compost bed height (1 m) and water content (50%).

The results of these studies are presented in Figure 4-8, where it is seen that the pressure drop increases significantly with increasing gas velocity for a bed of small particle size ($<1.2\text{ mm}$). For particles greater than 1.2 mm the pressure drop increases to a much lesser extent with increasing velocity as shown by a comparison of data for particle classes D and E. Clearly significant pressure drops observed in operating filter beds are a result of the presence of small particles with sizes less than 1 mm. For example, at a representative gas velocity of 0.03 m/s, which is equivalent to a loading rate of $110\text{ m}^3/\text{m}^2\text{-hr}$, the pressure drop realized by a 1-m bed of particles size classified as $<1.2\text{ mm}$ is 390 mm H_2O , whereas the pressure drop obtained for the same packing height and the same gas velocity, for particles classified as $>12\text{ mm}$ is only 2 mm H_2O . Thus, under these conditions the pressure drop created by 1 mm or less particles is about 200 times that caused by an equivalent bed composed of 12 mm or greater particles.



A: $d > 12$ mm
 B: $3.35 < d < 12$ mm
 C: $2.36 < d < 3.35$ mm
 D: $1.18 < d < 2.36$ mm
 E: $d < 1.18$ mm

Figure 4-8. Pressure drop as a function of particle size range for different gas velocities.

The relationships between pressure drop and packing height at constant gas velocity for particle size ranges B (3.33 to 12 mm) and E (<1.2 mm), and the parent compost #12 are shown in Figure 4-9. It is seen that the pressure drop increases approximately linearly with packing height for all three samples. It is important to note that the pressure drop values obtained for the parent compost are intermediate between the strong dependence of pressure drop on packing height for small particles (class E) and the weak dependence on packing height for larger particles (class B).

The dependence of pressure drop on compost water content is not as consistent as that for particle size. Qualitatively, sewage sludge treated compost contains more viscous and adhesive small particles than are found in untreated compost. Thus, when the water content of the sewage sludge treated compost is increased, coagulation of small particles is enhanced and the pressure drop increases sharply. However, the build-up in pressure may be suddenly released by channeling, i.e., a breakdown of the overall flow restriction by the formation of a channel of much less resistance caused by a separation of packed materials.

The effects of gas velocity on pressure drop across four typical biofilter materials are shown in Figure 4-10. As expected, the pressure drop increases rapidly with increasing gas velocity. The pressure drop depends on the way the filter is packed. Composts #12 and #13 are similar in nature but filter material #13 was more compacted than

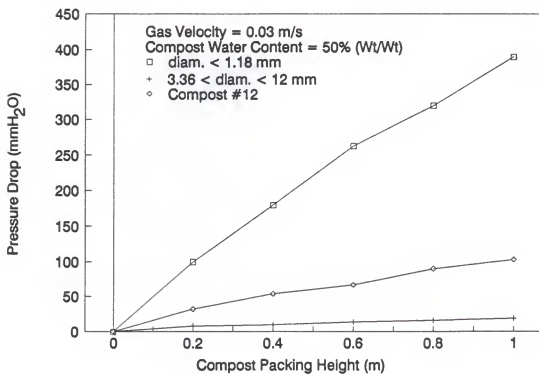


Figure 4-9. Pressure drop as a function of packing height for different compost particle size ranges.

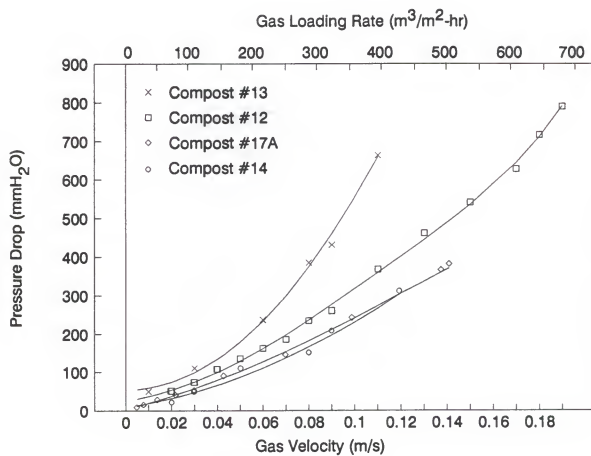


Figure 4-10. Pressure drop as a function of gas velocity for different types of compost.

#12, and the more densely packed material shows a much higher pressure drop for the same gas velocity. Composts #14 and #17A have similar pressure drop-gas velocity curves and although material #17A contains a larger fraction of small particles than does material #14 (see Table 4-3), the small particles in compost #17A are mainly sand and grass fractions, whereas those in compost #14 are sewage sludge particles, which tend to adhere to each other.

Effect of Gas Retention Time on H_2S Removal

The effect of gas retention time on H_2S reduction is studied by varying the gas flow rate through the tower. The results are presented in Table 4-4. In the first data set of 6 tests, the H_2S loading rate is kept approximately constant at a low flow range to ensure that the maximum H_2S elimination capacity of the system is not exceeded during the test. It is clear that there is no apparent effect on H_2S removal as long as retention times are longer than about 23 sec. When the retention time is reduced to 7 seconds, the H_2S removal efficiency decreases by about 6%. This decrease in H_2S is controlled by the macrokinetics of biofiltration process. Sublette and Sylvester (1987) reported that H_2S can be metabolized by a pure culture of *T. denitrificans* within 1-2 seconds. This suggests that the reduction of H_2S removal efficiencies under shorter residence times is not necessarily due to insufficient reaction time between the H_2S molecules and the biomass, but

Table 4-4. Effect of gas retention time on H₂S removal efficiency.

Gas Flow Rate (Lpm)	Reten. Time (s)	H ₂ S Loading Rate (g-S/m ³ -hr)	H ₂ S Inlet (ppmv)	H ₂ S Outlet (ppmv)	Removal Eff. (%)
151	7.06	16.3	24.9	1.62	93.5
106	9.98	17.1	37.0	1.30	96.5
75.5	14.1	17.7	53.7	0.77	98.6
46.0	23.1	21.0	105	0.30	99.7
30.8	34.5	20.7	155	0.02	99.9+
15.3	70.0	19.8	297	0.01	99.9+
15.0	71.0	39.8	610	BDL	99.9+
15.0	71.0	50.7	776	2.77	99.6
9.00	118	56.3	1440	0.01	99.9+
9.00	118	73.2	1870	4.24	99.8
5.40	197	62.3	2650	4.58	99.8

is possibly due to the slower step of H_2S diffusion from the gas phase into the liquid phase.

In the second data set of 5 tests presented in Table 4-4, the biofilter inlet gas contains very high H_2S concentrations and the system is operated at lower flow rates and, therefore, longer retention times. These tests show that, even when the inlet gas contains an H_2S concentration of 2650 ppmv, the biofilter can successfully reduce the concentration to 4.6 ppmv with a 99.8% removal efficiency when the retention time of the flowing gas is increased to 197 seconds. Thus, it can be seen that, as long as the H_2S loading rate does not exceed the maximum H_2S elimination capacity of the system (discussed in a later section), then the design engineer or operator can always deal with high H_2S concentrations in the waste gas by decreasing the gas flow rate to obtain the desired high level of control efficiency.

Effect of Concentration of H_2S on Its Removal

The effect of H_2S concentration in the inlet gas on the H_2S removal efficiency has been investigated under constant gas flow rate conditions. The results of these studies are presented in Table 4-5. No significant difference in control efficiencies is observed when H_2S concentrations in the influent gas stream are varied from 5.5 ppm to 518 ppm as long as the H_2S loading rate is less than the maximum acceptable value for the compost studied.

Table 4-5. Effect of H₂S concentration on removal efficiency.

Gas Flow Rate (Lpm)	Reten. Time (s)	H ₂ S Loading Rate	H ₂ S Inlet (ppmv)	H ₂ S Outlet (ppmv)	Removal Eff. (%)
		(g-S/m ³ -hr)			
30.0	35.4	0.72	5.51	BDL	99.9+
30.4	35.0	1.69	12.8	BDL	99.9+
30.8	34.5	16.9	126	0.01	99.9+
30.8	34.5	26.3	196	1.31	99.3
30.0	35.4	29.6	227	0.01	99.9+
30.0	35.4	38.1	292	0.01	99.9+
31.2	34.0	70.4	518	1.04	99.8

Effect of H₂S Loading Rate on Its Removal

One of the most important observations made in this study is the relationship between H₂S reduction and its loading rate to the biofilter. It is very important and necessary to introduce here the concept of H₂S loading rate and the maximum elimination capacity of the filter material. The H₂S loading rate is the amount of H₂S that is being introduced to the system per unit volume of the packing material per unit time (g-S/m³-hr). The maximum elimination capacity of a compost is the maximum H₂S loading rate that the compost can bear without inhibiting its microbial activity, and is expressed in the same units as those used for H₂S loading rate. These two parameters probably play central roles in biofilter design and system operation.

The maximum H₂S elimination capacity of a compost depends on the microbial population and activity of sulfur oxidizing bacteria existing in the compost. The latter, in turn, are related to the operating conditions of the system, such as temperature, water content, acidity (pH) of compost, and the concentrations of nutrients and inhibitory substances.

Overloading of the biofilter system with H₂S is indicated by the appearance of a finely divided, yellowish-white colored substance on the compost, a sudden decrease in the H₂S removal efficiency or the occurrence of higher concentrations of elemental sulfur in the compost.

The maximum H_2S elimination capacity for a compost is determined at the optimum operating conditions of the system. H_2S concentrations in the inlet gas stream are varied increasingly at a constant gas flow rate. The H_2S removal rates ($g-S/m^3-hr$) are plotted v.s. the H_2S loading rates ($g-S/m^3-hr$). The maximum H_2S elimination capacity of the compost is determined when the curve flattens out (Ottengraf, 1986). The maximum H_2S elimination capacity of compost #13 is determined to be $11.5 g-S/m^3-hr$ (Figure 4-11). The maximum H_2S elimination capacity of this compost is very low because its extremely low pH (1.60) and high sulfate content ($70.4 mg-S/g$, see Table 4-2).

The maximum H_2S elimination capacity for a compost can also be determined through kinetics studies. Detailed information is presented in the section of "Kinetics of H_2S Oxidation in a Biofilter". The maximum H_2S elimination capacity for compost #17 is determined to be $129 g-S/m^3-hr$.

Effect of Compost Water Content on H_2S Removal

The effect of compost water content (CWC) on H_2S removal was evaluated using the Column System #4. The compost (Compost #17) which was used for this study and other studies carried out using Column System #4 had been previously packed in Tower #2 and was considered to be pre-conditioned by H_2S to a stable operating condition. After transfer to System #4, the compost was operated at the same conditions as used in its parent environment, Tower #2,

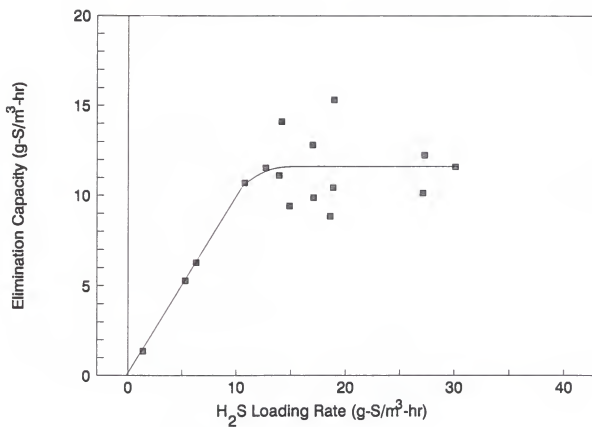


Figure 4-11. Determination of maximum H₂S elimination capacity of compost.

before changing the operational parameters. No change in H_2S removal capacity was found due to the system transfer. Data were not taken until system #4 reached a stable condition after any changes in the operational parameters or conditions were made. Each column in System #4 was packed with equal weights of compost. The range of compost water contents evaluated was from 0%, oven dried compost, to about 62%, the maximum water holding capacity of the compost. Water content of the compost in each column was adjusted to a desired range by either adding DI water to the compost or by gently drying the compost in room air. One of the composts tested was thoroughly dried in an oven at $110\text{ }^{\circ}\text{C}$ for 24 hours to obtain water free compost. The system was operated at room temperature with a gas loading rate of about $15\text{ m}^3/\text{m}^2\text{-hr}$. Inlet H_2S concentrations were controlled in a range between 80 and 110 ppmv. The results are illustrated in Figure 4-12.

The H_2S removal efficiency was maintained at a high value, 99.9+%, with little variation being observed when the CWC was varied from 30% to 62%. When the CWC was reduced below 30%, the H_2S removal efficiency decreased linearly with the CWC. Very little removal of H_2S was observed for the oven dried compost. The residual efficiency of the latter is probably due only to chemical oxidation and adsorption of H_2S on the compost.

Water is essential for all living organisms. All biological metabolic processes require water as a medium or

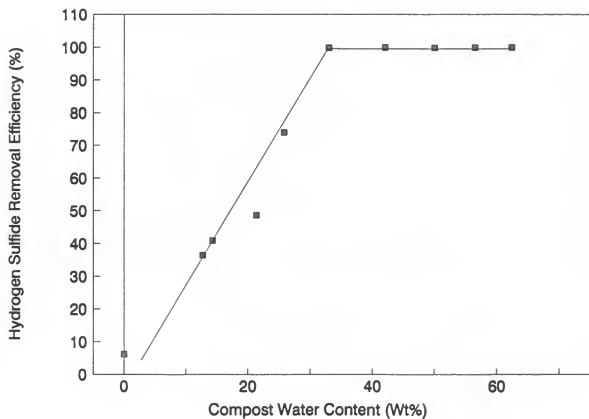


Figure 4-12. Effect of compost water content on H_2S removal efficiency.

solvent. Insufficient water supply can limit the activity of the microorganisms, which in turn reduces the H_2S oxidation rate. It is also possible that when the CWC reduced below 30%, there is no free water existing in the pores of the compost particles. This may decrease the rate of transfer of H_2S from the waste gas to the biofilm where the biological oxidation of H_2S takes place.

Biological activity of the "dry" compost can be recovered if water is supplied to the compost to bring the CWC to a proper range. Two composts, WCF4 and WCE3 with original CWCs of 14.3% and 21.4%, respectively, were used to study this phenomenon. DI water was added to bring the water contents of composts WCF4 and WCE3 to 56.5% and 50%, respectively. The biological activity of both composts as indicated by H_2S removal was recovered eventually up to 99.9+%. The time required for recovery of the activity, however, is inversely proportional to the dryness of the "dry" compost. As shown in Figure 4-13, it takes 63 hours for compost WCF4 to recover its H_2S removal efficiency to 99.9+% while compost WCE3 took 41 hours to reach the same level even though both systems followed a similar recovery pattern.

Effect of Compost Acidity on H_2S Removal

The effect of compost acidity on H_2S removal was investigated using the Column System #4. The source of the compost is the same as described in the previous section.

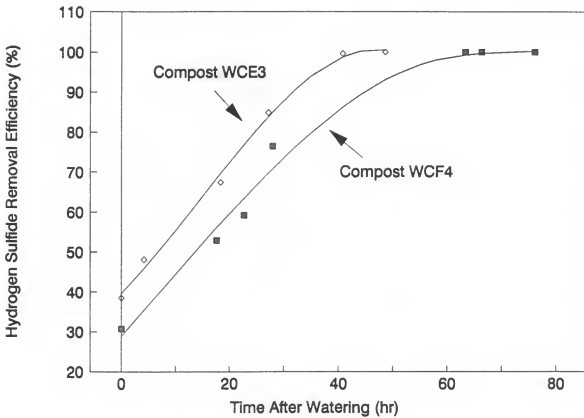


Figure 4-13. Time required for dried compost to recover optimum efficiency.
Original compost water content:
WCE3 = 21.4%,
WCF4 = 14.3%.

The compost used in each column was treated with either dilute HCl or dilute NaOH solutions to bring the pH of the compost to a desired range. The final pH values obtained for the composts studied in each column are 1.57, 3.20, 4.42, 5.02, 6.39, 6.75, and 8.76, respectively. Measurements of inlet and outlet gas sample concentrations were made when the bed operation became stable. The results of these studies are shown in Figure 4-14. Repeated measurements at each pH point are used to estimate the mean value, and mean $\pm$ 2 standard deviations values (error bars) indicated by the upper and lower bounds of the vertical line through the mean. Two operational conditions are used in this test. Under condition A, lower H_2S and gas loading rates are used. No significant effect of pH of compost on H_2S removal is observed for pH values in the range between 3.2 and 8.76. Removal efficiencies of 99.5+% are consistently determined with little or no variation in this range. When the pH was reduced to 1.57, the H_2S removal efficiency fell sharply to about 9%. It should be noted that the measured H_2S removal efficiencies showed larger variations at the lower pH range. Following the previous studies, the operational conditions were changed to condition B. Under the latter conditions, higher H_2S and gas loading rates were used and the effects of varying pH the compost becomes evident. It can be seen in Figure 4-14, condition B, that the maximum H_2S removal occurred at a compost pH value of 3.2 (99.2%). The removal efficiency

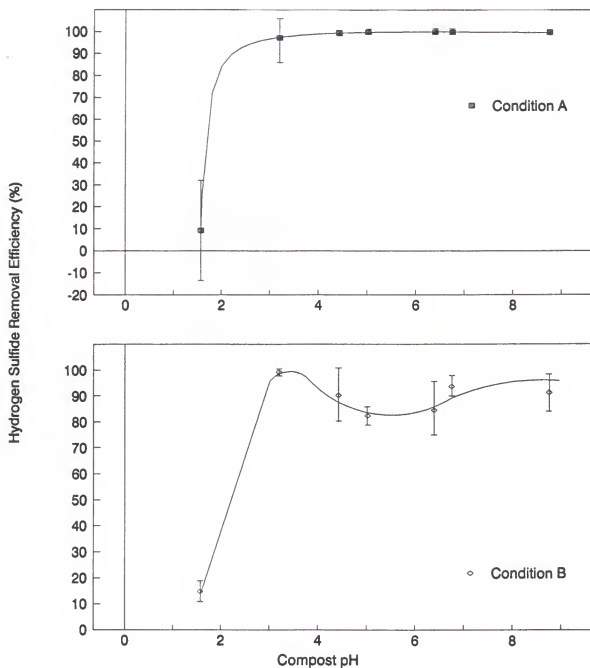


Figure 4-14. Effect of compost pH on H_2S removal efficiency.

Condition a:

H_2S loading rate: $10.5 \text{ g/m}^3\text{-hr}$

Gas loading rate: $15 \text{ m}^3/\text{m}^2\text{-hr}$

Condition b:

H_2S loading rate: $35.4 \text{ g/m}^3\text{-hr}$

Gas loading rate: $26.1 \text{ m}^3/\text{m}^2\text{-hr}$

decreased with decreasing acidity up to pH 5 (82.3%), and then increased with further decrease in acidity of the compost. As discussed previously in Chapter 2, sulfur oxidizing bacteria can live in environments with a wide pH range (1-8) depending on the species present. Probably the dominant species present in the biofilter systems studied are acidophiles which prefer an optimum pH value around 3. For the higher pH value range, chemical reaction between H_2S and the compost material can significantly enhance its removal in addition to biological oxidation. As a result of this dual action, higher removal efficiencies of H_2S can be expected.

The acidity of the compost is traditionally expressed as 'compost pH' for convenience. A more meaningful and accurate way to express the compost acidity is the 'specific acidity of compost (SAC)', which gives the quantity of H^+ per unit weight of dry compost, $\mu g-H^+/g$. Specific acidity of compost can be calculated from compost pH by the following equation:

$$SAC = W/[C_w(100-CWC)] \times 10^{5-pH} \quad (4-1)$$

where:

SAC = specific acidity of compost, $\mu g-H^+/g$ -dry compost
 W = DI water used for compost pH analysis, mL
 C_w = Weight of wet compost used for pH analysis, g
 CWC = Compost water content, Wt%
 pH = compost pH.

For example, if 2g of wet compost is taken and 20 mL of DI water is used in H^+ extraction for a compost pH analysis,

and the compost water content is 60% by weight, providing a compost pH of 1.57, then the dry specific acidity of this compost is:

$$\text{SAC} = 20/[2(100-60)] \times 10^{5-1.57} = 673 \text{ } (\mu\text{g-H}^+/\text{g}).$$

Effect of Temperature on H₂S Removal

The effect of temperature on H₂S removal efficiency was studied using Column System #4 with some minor modifications. The modified system is shown in Figure 4-15. Three columns (triplicate) packed with the same compost were placed in a heating box. A rheostat was used to control the temperature of the columns. The influent gas stream was blown through a bubbler, which is placed in a water bath and heated up to the same or slightly higher (5°C) temperature as the biofilter columns to saturate the gas stream at the desired temperature. For tests carried out below room temperature (22°C), the reaction columns were placed in a refrigerator and the temperature adjusted through the refrigerator thermostat. The temperature range investigated is between -1.5 to 103°C. The results of the triplicate measurements for each temperature point are plotted means and ± 2 standard deviations as error bars in Figure 4-16.

In the range from 25°C to 45°C, high H₂S removal efficiencies are consistently observed with little variation. The H₂S removal efficiency, however, dropped rapidly with decreasing temperature in the lower temperature

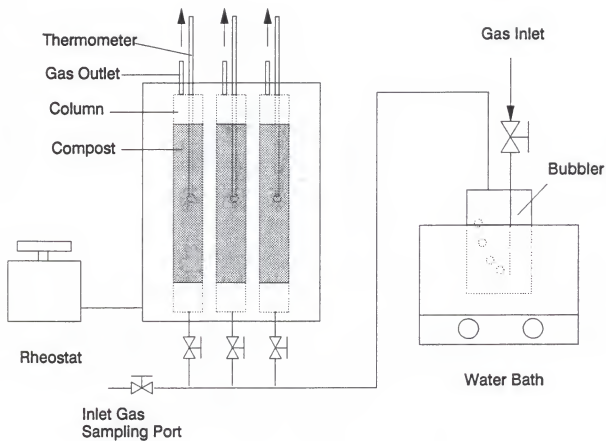


Figure 4-15. Schematic drawing of the experimental arrangement for investigation of the effect of temperature on H_2S removal efficiency.

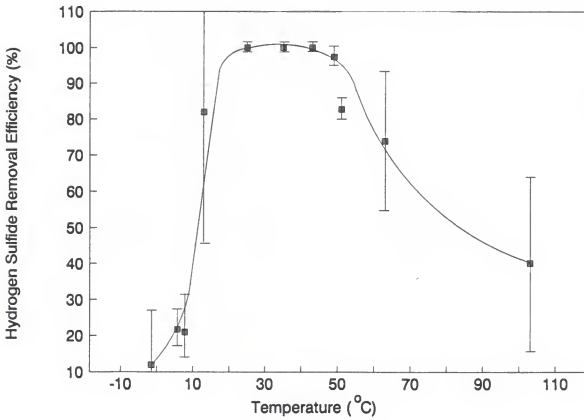


Figure 4-16. Effect of temperature on H₂S removal efficiency.

range. For instance, when the temperature was reduced from 25°C to 7.5°C, the removal efficiency decreased by approximately 80%. At 7.5°C, only 20% removal efficiency was observed. On the other hand, the decrease in H₂S removal in the higher temperature range was less marked than observed at lower temperatures. For example, when the temperature was increased from 50°C to 100°C, the H₂S removal efficiency decreased from 97.4% to 40%. The optimum temperature range determined from these studies is between 30°C and 40°C, which is the optimum temperature range for mesophilic bacteria. The removal rates of H₂S at high temperature is probably due to chemical oxidation reactions in addition to biological oxidation.

Poor performance of a biofilter at low temperatures may limit their application in cold climates, especially during the winter. Proper means should be taken to avoid operating biofilter systems below 10°C. For larger biofilters, the bed temperature can be a few degrees higher than the ambient air temperature due to biological respiration of the microbes and the exothermal oxidation reactions in the filter. Kampbell et al. (1987) reported that soil bed biofilter functioned well at temperatures in the range 12°C to 24°C in Wisconsin. In another study carried out by Rands et al. (1981) the filter bed temperatures were found to be 10 to 20°C higher than ambient air temperatures during winter times. This type of thermal enhancement, however, was not observed during this study, probably because the

system is not large enough to maintain an adiabatic condition.

Effect of Sulfate on H₂S Removal

The effect of sulfate presence on H₂S removal was evaluated using Column System #4. A preconditioned stable compost from Tower #2 was divided into 8 equal-weight portions. Two of the sub-composts with an original sulfate content of 4.6 mg-S/g were packed directly into two columns as controls. The other sub-compost portions were mixed with sodium sulfate (Na₂SO₄) to bring the compost sulfate content to 24.6, 44.6, 64.6, 84.6, 104.6 and 204.6 mg-S/g, respectively, and packed in the other 6 columns. After a few days for acclimation, H₂S removal efficiencies for each column were determined. The system was operated at a gas loading rate of 15 m³/m²-hr and an H₂S loading rate between 6.6 and 8.4 g-S/m³-hr. The results are illustrated in Figure 4-17.

No effect is observed when the compost sulfate content is less than 25 mg-S/g. However, a significant effect is observed at higher sulfate levels. The H₂S removal efficiencies were reduced from 99.94% to about 35% and remained in the lower removal efficiency range when the sulfate content was increased from 45 to 200 mg-S/g. These results suggest that a sulfate content of 25 mg-S/g is a critical level for the microbial environment. Above this level sulfate probably reaches a toxic level and the

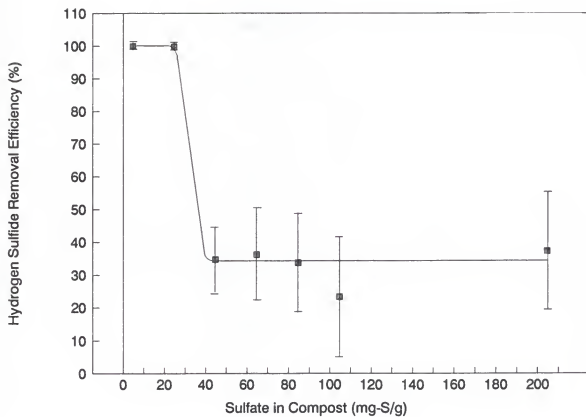


Figure 4-17. Effect of sulfate on H₂S removal efficiency.

activity of these microorganisms is markedly inhibited. This observation is very important for biofiltration control of H_2S . Since sulfate is the final product of the biofiltration process, it may accumulate in the biofilter bed if no other action is taken. Accumulation of sulfate can easily reach a level that can significantly reduce the function of the biofilter. Measures to avoid sulfate accumulation in filter and to enable recovery of the deteriorated compost are discussed in Chapter 5.

Effect of Nutrient Addition on H_2S Removal

Low and high sulfur-containing composts were used for investigation of the effects of nutrient addition on H_2S removal. The total-S contents are 17.5, 33.7, 20.2 and 119.7 mg-S/g for compost A, B, C, and D, respectively. Each compost was packed in two columns, one is used as a control, and the other was treated with nutrients. Fifty (50) mL of nutrient solution was mixed with 140 g of the compost tested in each column. Excess water was removed by exposing the compost to room air for 24 hours. The nutrient added is similar to the enrichment medium for sulfur-oxidizing bacteria suggested by Aaronson (1970). The composition of the solution is: K_2HPO_4 , 1.0 g; $MgSO_4 \cdot 7H_2O$, 0.5 g; NH_4NO_3 , 1.0 g; $CaCO_3$, 10 g, and DI water was added to bring the final volume to 1000 mL.

The results on the effect of nutrient addition on biofilter performance are presented as a bar graph in Figure

4-18. For each compost set, H_2S removal efficiencies are plotted for the control compost and the test compost before and after the addition of nutrient solution. It can be seen that the H_2S removal efficiencies are significantly decreased for the three composts tested with low sulfur content when the nutrients are added. The reason for this decline in efficiency is not clear. No improvement of H_2S removal for the high sulfur containing compost was observed, either.

Kinetics of H_2S Oxidation in a Biofilter

Theoretical Considerations

In general, the substrate utilization rate of a component by microbial flora as well as the enzymatic reaction rate are expressed by the Michaelis-Menten relationship (White et al., 1978; McGilvery and Goldstein, 1983; Schmidt, et al., 1985):

$$-dC/dt = V_{\max}CB/(K_m + C) \quad (4-2)$$

where C is the substrate concentration, B is the population density, $V_{\max}$ is the theoretical maximum specific reaction rate, K_m is the half-saturation constant (Michaelis constant), and t is the reaction time.

Under steady state conditions, i.e., when the microbial population does not change with time, there are three situations which may be encountered in a biological reaction system, and corresponding equations can be derived, from

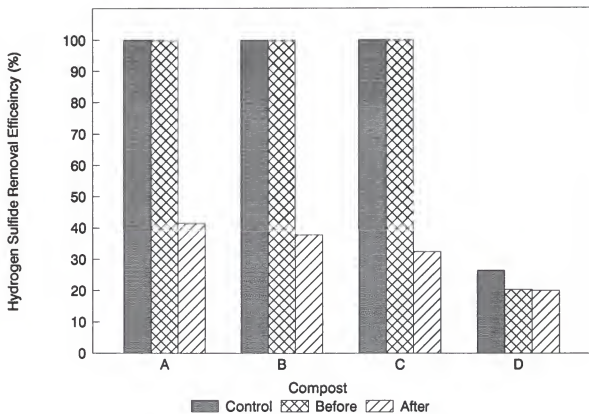


Figure 4-18. Effect of nutrient addition on H_2S removal.

Total-S content in compost (mg-S/g)

A: 17.5

B: 33.7

C: 20.2

D: 120

equation 4-2 above, to express the rates of biological reaction for each particular situation:

1) If the substrate concentration is very high, i.e., when $K_m \ll C$, the rate expression approaches zero-order kinetics in the substrate concentration:

$$-dC/dt = V_{\max}B = k_0 \quad (4-3)$$

where k_0 is a zero-order rate coefficient. The integral form of equation 4-3 becomes:

$$C = C_0 - k_0 t \quad (4-4)$$

where C_0 and C are the initial substrate concentration and the substrate concentration at time t , respectively.

If $C_0 - C$ is plotted against t , a straight line should be obtained and the slope k_0 is the maximum elimination capacity of the microbes for the substrate.

2) If the substrate concentration is very low, i.e., when $C \ll K_m$, a first-order kinetics dependence should be obtained:

$$-dC/dt = k_1 C \quad (4-5)$$

The integral form for equation 4-5 becomes:

$$C = C_0 \exp(-k_1 t) \quad (4-6)$$

where k_1 is the first-order reaction rate coefficient.

If $\ln(C/C_0)$ is plotted against t , a straight line should be obtained and the first-order reaction coefficient,

k_1 , can be determined from the slope of the line.

3) In the third situation, when the half-saturation constant, K_m , and the substrate concentration, C , are comparable, the biological reaction should follow fractional order kinetics, because equation 4-2 can not be simplified. Relatively complex equations have to be derived to express the fractional order kinetics.

A number of theoretical and empirical models have been reported which describe the kinetics of biodegradation of organic compounds and reduced sulfur species (Chen and Morris, 1972; Williamson, 1973; Cooper, 1974; Jennings et al., 1976; Williamson and McCarty, 1976a,b; O'Brien and Birkner, 1977; Rittmann et al., 1978; Schmidt et al., 1985; Kampbel et al., 1987; Caunt and Hester, 1989). In particular, Ottengraf and coworkers have published a series of papers that describe the processes involved in the operation of biofilters (Ottengraf and Van Den Oever, 1983; Ottengraf et al., 1984; Ottengraf, 1986; Ottengraf et al., 1986; Ottengraf, 1987). Ottengraf developed a biophysical model as well as derived mathematical solutions to describe the kinetics of biodegradation of various organic compounds in biofilter systems.

As described previously in chapter 2, Ottengraf's model uses the concept of a bed consisting of solid filter particles, where each particle is surrounded by a wet, biologically active layer. When waste air flows around the particle there is continuous mass transfer of pollutant from

the gas phase to the biolayer (See Figure 2-3).

The overall kinetic behavior observed in a biofilter is a result of the interaction between mass transfer phenomena, the microkinetics of the biological elimination reactions, the residence time distribution of the gas flow, etc.. This overall kinetic behavior is termed 'macrokinetics' by Ottengraf and can be determined experimentally.

Ottengraf divided the macrokinetics in a biofilter into two classes: first-order reaction and zero-order reaction. He expressed the first-order reaction kinetics in a form similar to equation 4-4 described previously. For zero-order reaction kinetics, however, Ottengraf has distinguished the following two situations:

1. At gas phase concentrations, C , above a compound specific, critical concentration (C_{crit}), the film will be fully saturated (Figure 2-3, Case 1) and pollutant elimination is limited by the biological activity in the biofilm. This process is defined as reaction limitation.
2. At concentrations less than C_{crit} , diffusion in the biofilm will limit compound removal. The biofilm is no longer fully penetrated (Figure 2-3, Case 2) and the removal rate decreases with decreasing pollutant concentration in the waste gas. This process is referred to as diffusion limitation.

Ottengraf has also derived two equations which describe the kinetics for either situation.

For the first situation, i.e. under reaction limiting conditions, the kinetics expression is:

$$C/C_0 = 1 - K_O H / C_0 U_g \quad (4-7)$$

where C is the effluent gas concentration, C_0 is the influent gas concentration, H is the height of the filter bed and U_g is the gas velocity. This equation is a different way of expressing equation 4-4, specifically for a biofilter.

Under diffusion limiting conditions, the kinetics expression is:

$$C/C_0 = [1 - (H/U_g)(K_0 D_e a / 2m C_0 \delta)^{1/2}]^2 \quad (4-8)$$

where a is the interfacial area per unit volume, D_e is the effective diffusion coefficient, m is the distribution coefficient of the component, and δ is the biolayer thickness.

Determination of the Kinetics of H_2S Oxidation in a Biofilter

Hydrogen sulfide elimination rates are measured when the biofilter has reached a steady state conditions. Gas samples are taken at different locations along the tower and the H_2S concentrations in the gas samples are analyzed. The initial H_2S concentrations, C_0 , in the inlet gas stream are varied from low to high values in order to determine the kinetics under different situations as described in the previous section. The results for compost #17 packed in Tower #2 are presented in Figures 4-19, 4-20, 4-21, 4-22, and 4-23.

Under high H_2S concentrations in the inlet gas stream ($H_2S > 400$ ppmv), the reaction appears to follow zero-order

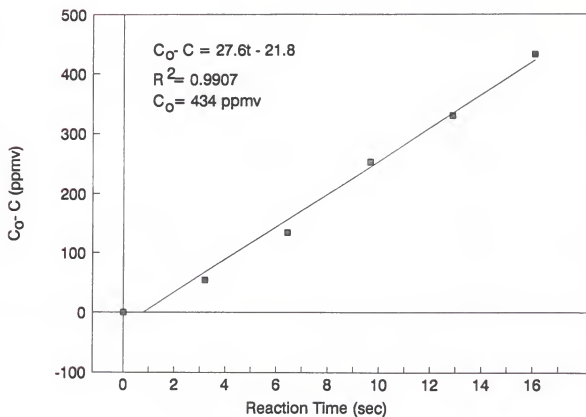


Figure 4-19. Linear least squares regression analysis for zero-order kinetics of H_2S oxidation in biofilter. Gas loading rate: $224 \text{ m}^3/\text{m}^2\text{-hr}$, compost #17.

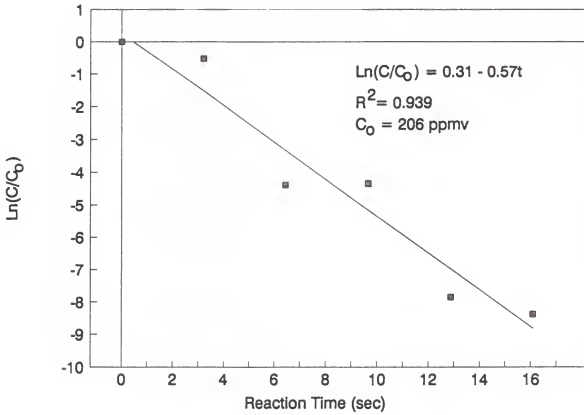


Figure 4-20. Linear least squares regression analysis for first-order kinetics of H_2S oxidation in biofilter. Gas loading rate: $224 \text{ m}^3/\text{m}^2\text{-hr}$, compost #17.

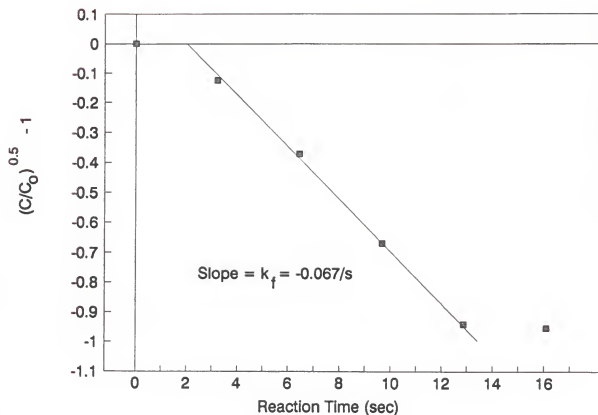


Figure 4-21. Determination of the fractional-order reaction rate coefficient, k_f by linear least squares regression. Gas loading rate: $224 \text{ m}^3/\text{m}^2\text{-hr}$, compost #17.

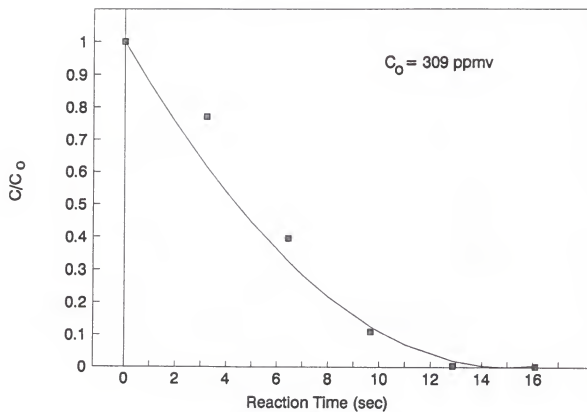


Figure 4-22. Plot showing the fractional-order kinetics of H_2S oxidation in biofilter. Gas loading rate: $224 \text{ m}^3/\text{m}^2\text{-hr}$, compost #17.

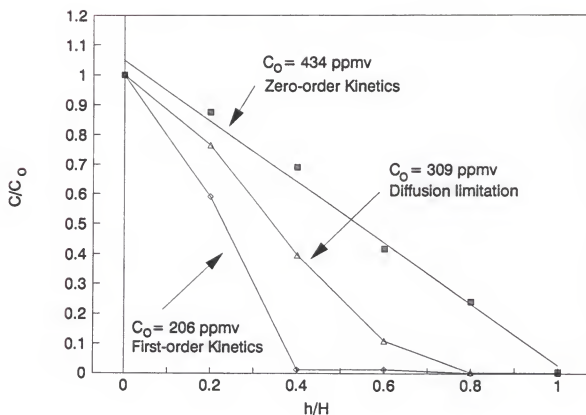


Figure 4-23. Concentration profiles for H_2S as a function of packing height within the biofilter. Gas loading rate: $224 \text{ m}^3/\text{m}^2\text{-hr}$, compost #17.

kinetics according to equation 4-4 (Figure 4-19). The regression formula is expressed as:

$$C = C_0 - 27.6t + 21.8 \quad (4-9)$$

with a correlation coefficient R^2 of 0.9907. The good agreement obtained supports the conclusion that the reaction can be described by zero-order kinetics. The value obtained for K_0 is 27.6 ppmv/s. This zero order coefficient corresponds to a maximum H_2S elimination capacity of 130 g-S/m³-hr for the compost at the operating conditions selected. It should be noted that the second and third data points in Figure 4-19 are below the regression curve. This deviation is mainly due to the H_2S removal efficiency in the lower portion of the filter has been effected by high acidity and sulfate content in the compost in this portion of the bed as a result of prolonged operation.

For lower inlet H_2S concentrations ($H_2S < 200$ ppmv), the reaction appears to follow first-order kinetics as expressed by equation 4-6 (Figure 4-20). The linear regression formula is expressed as:

$$\ln(C/C_0) = 0.31 - 0.57t \quad (4-10)$$

In this case the value for k_1 is 0.57/s, which is applicable for inlet H_2S concentration of less than 200 ppmv.

When H_2S concentrations fall in the intermediate range, i.e., between 200 ppmv and 400 ppmv, the data cannot be

represented by either Equation 4-4 (zero-order kinetics) or equation 4-6 (first-order kinetics). Several empirical equations have been tested, and Ottengraf's diffusion limiting model was found to be the most accurate expression describing H_2S oxidation kinetics in this range for the operating conditions employed.

In order to conveniently use Ottengraf's model, and equation 4-8, however, it is necessary to define a new parameter, the fractional-order reaction coefficient k_f :

$$k_f = (k_o D_e a / 2 m_i C_o \delta)^{\frac{1}{2}} \quad (4-11)$$

It can be seen that k_f is a function of the operating conditions of the biofilter system, and under steady state conditions, k_f is constant.

Thus, equation 4-8 can be rewritten as:

$$C/C_o = (1 - k_f t)^2 \quad (4-12)$$

or

$$(C/C_o)^{\frac{1}{2}} - 1 = -k_f t \quad (4-13)$$

where $t = H/U_g$ is the reaction time.

When $(C/C_o)^{\frac{1}{2}} - 1$ is plotted against t , a straight line should be obtained, and the slope of the line should equal k_f . A sample plot of the relation in equation 4-13 for the concentration range 200 to 400 ppmv H_2S is shown in Figure 4-21. The reasonableness of this plot supports the concept of fractional-order dependence in the stated range of concentrations.

Thus, it appears that equation 4-12 can be used to predict the kinetics of H_2S oxidation in the intermediate H_2S concentration ranges.

A set of experimental data ($H_2S = 309$ ppmv) are plotted in Figure 4-22, where the symbols used are experimental data points, and the solid curve is drawn according to equation 4-12. It can be seen that the experimental data are adequately described by the diffusion limitation model.

The data shown in Figures 4-19, 4-20, and 4-22 are plotted in Figure 4-23 in the "Ottengraf-form", i.e., C/C_0 on the y-axis and h/H on the x-axis, where h is the height of sampling location on the filter and H is the total height of the filter. It is informative to use this plot in order to observe the H_2S concentration profile in the biofilter.

According to Ottengraf, under reaction limiting conditions, a straight line should be obtained for this type of plot. However, the profile is no longer linear if the substrate elimination rate is controlled partially or completely by the diffusion rate in the biofilter. The latter feature is clearly observed in this study of H_2S elimination. The data that are plotted in Figure 4-20 shows a straight line in Figure 4-23. This linear relation is an indication of zero-order kinetics and reaction limiting control by the microbial population. When inlet H_2S concentrations are less than 434 ppmv (the middle curve), the profile is curved (concave) below the straight line, indicating that the reaction is partially diffusion

controlled at intermediate H_2S concentrations. With further lower H_2S concentrations, the profile becomes curved well below the straight line, and suggests that the dominant mechanism is diffusion limited in this first-order kinetics region.

Table 4-6 summarizes the equations describing the kinetics of H_2S oxidation in the biofilter system. These equations allow for a quantitative description of the basic processes involved in this biofiltration elimination of H_2S and they allow for an accurate sizing of biofilters for H_2S removal. It should be noted that the macrokinetics of H_2S oxidation in biofilters as well as the reaction coefficients reported here are related to operational conditions. The kinetics are valid for a similar compost biofilter system operating under similar conditions. If operational conditions such as pH, temperature, sulfur content, etc. are changed, then the kinetic behavior may be altered. In practice, the kinetic behavior for a particular compound should be determined by laboratory or pilot scale studies (Van Lith, 1989; Leson and Winer, 1991).

Table 4-6. Models for the kinetics of H₂S oxidation in biofilter.

H ₂ S Concen. Range (ppmv)	Kinetic Order	Reaction Coefficient	Equation
<200	First	$k_1 = 27.6/\text{s}$	$-\text{d}C/\text{d}t = k_1 C$ $C = C_0 \exp(-k_1 t)$
200-400	Fractional	$k_f = 0.067/\text{s}$	$C = C_0 (1 - k_f t)^2$
>400	Zero	$k_0 = 0.567 \text{ppmv}/\text{s}$	$-\text{d}C/\text{d}t = k_0$ $C = C_0 - k_0 t$

CHAPTER 5
BIOFILTER PERFORMANCE AND CHANGES IN COMPOST PROPERTIES
ASSOCIATED WITH LONG TERM OPERATION

Towers #1 and #2 were packed with composts #17A and #17, respectively, and operated continuously for more than 200 days. Tower #3 was packed with compost #16 and operated for 130 days. Long term performance of these biofilter tower systems for H_2S removal and changes in compost properties are reported here. Biofilter maintenance conditions and recommended procedures for developing optimum performance have been determined through these long term observations.

Overall Performance of the Biofilters

The overall performance of Towers #1, #2 and #3 are presented graphically in Figures 5-1, a, b and c, respectively. In each figure, H_2S loading rates, inlet/outlet H_2S concentrations and H_2S removal efficiencies are plotted against the cumulative operation time. Except for some specific tests, where extreme operating conditions were used (such as high H_2S loading rate, high gas flow rate, etc) and data are presented and discussed elsewhere, the data showed in these figures are daily averages for an individual day when the measurements were made. Usually, Towers #1 and 2 were operated at a gas loading rate of 100

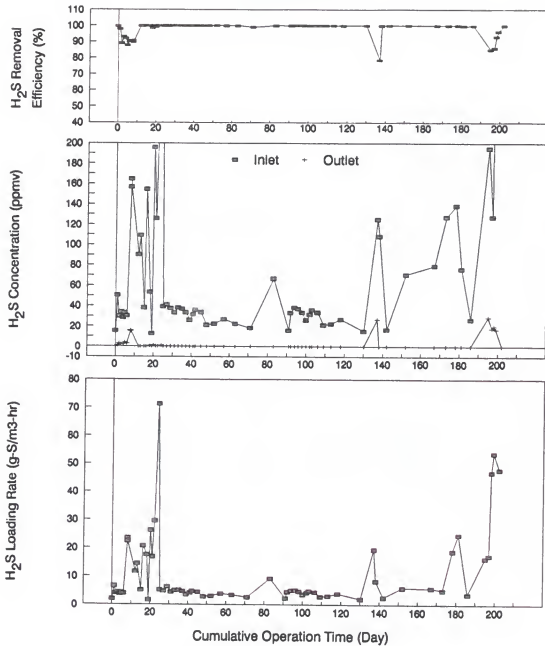


Figure 5-1. Biofilter control of H₂S during long term operation.
a) Tower #1, compost #17A.

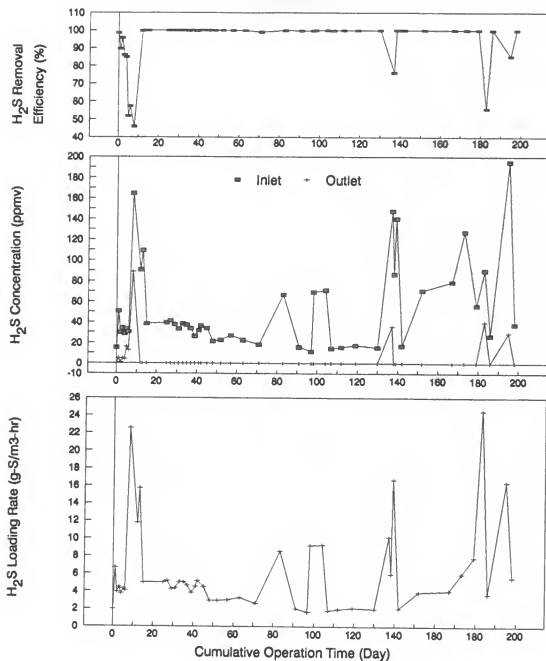


Figure 5-1. Biofilter control of H₂S during long term operation.
b) Tower #2, compost #17.

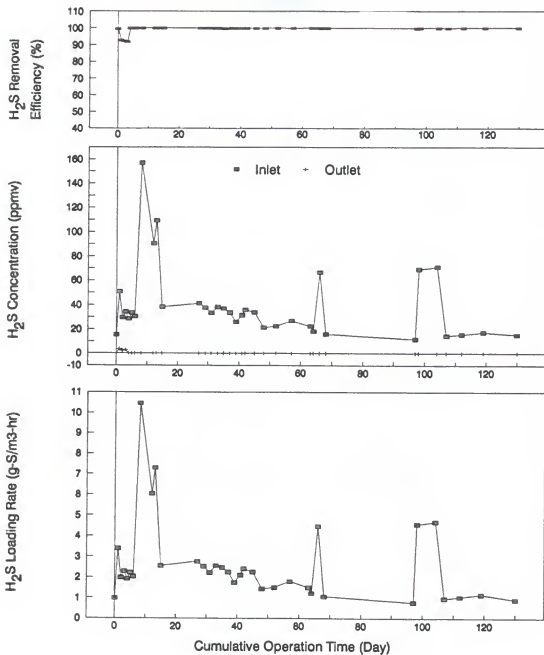


Figure 5-1. Biofilter control of H₂S during long term operation.
c) Tower #3, compost #16.

$\text{m}^3/\text{m}^2\text{-hr.}$

All three composts studied showed very good overall performance characteristics during continuous long term operation. The acclimation periods for all three composts are similar, approximately 10 days. After this period, the filters achieved stable operating conditions.

Tower #3 was operated under a lower gas loading rate, $50 \text{ m}^3/\text{m}^2\text{-hr}$ (Figure 5-1c). This tower was not washed during 130 days of operation. When unpacked, the color of the compost at the bottom of the tower (inlet) had changed to yellowish-white, indicating accumulation of sulfur. The compost at the bottom of the tower was wet, with a water content of 55.9%, but the compost became drier as samples were analyzed at various distances up the tower. The water content of the compost in the top portion of the biofilter (exit) was only 25.8%. This characteristic is probably common for closed biofilter systems with no additional water supplied to the system except water contained in the influent gas stream. Although the gas is prehumidified and almost saturated with water ($\text{RH} > 95\%$) at ambient temperature, the temperature in the compost can be a few degrees ($^{\circ}\text{C}$) higher than the incoming gas stream due to the exothermic oxidation reactions occurring in the system and the biological respiration of the biomass. The rise of compost temperature is more significant with high H_2S loading rates. The elevated bed temperature causes the gas stream to become more unsaturated, and results in loss of

water by evaporation from the compost. Drying-out of the compost, therefore, is a natural feature of any biofilter system. The drying-out process may be slower for those biofilters which are used to remove hydrocarbons because water is one of the products of the biodegradation reactions. There is no water formed during the biological oxidation of H_2S . As a result, water has to be added to the system at the effluent end of the bed to keep the compost water content constant.

Towers #1 and #2 are packed with the same compost (#17) except that 2% by weight of $CaCO_3$ was added to the compost packed in Tower #1 (Compost #17A) as a pH buffer. It should be noted that the addition of $CaCO_3$ did not affect the performance of the biofilter.

These two towers have been packed and operated since January 29, 1991. Both of these towers have been subjected to large variations in waste gas surface loading and H_2S loading rates during the operation period because the effects of these variables on H_2S removal efficiencies were evaluated in this dual-tower system. High H_2S removal efficiencies and stable performance, were consistently observed.

The composts (#17 and #17A) showed good moisture retention and buffering capacity. In addition to the water added by pre-humidification of the inlet gas stream, these two towers were washed biweekly using DI water. The latter procedure was performed to keep the compost water content in

the desired range. The main purpose of this procedure, however, is to reduce the acidity and prevent accumulation of sulfate in the compost. A typical compost water content distribution profile in Tower #2 is presented in Figure 5-2. Samples were taken and analyzed before washing (14 days after the last washing) and 1 hour after washing the tower.

It can be seen that 1) the water content of the compost is evenly distributed along the length of the bed, and 2) the compost has very good water retention and buffering capacity. Only 3-5% of the compost water content was lost during the 14 day interval between washings. When the biofilter tower was operated for 130 days and samples were taken and analyzed, the water holding capacity of the compost in the inlet region had decreased slightly compared to that in the outlet region.

The system showed a good buffering capacity to gas surface loading changes. No significant reduction in H_2S removal efficiency was observed when the gas surface loading rate was varied in the range 20 to $500 \text{ m}^3/\text{m}^2\text{-hr}$ for the same H_2S loading rate.

Also, the buffering capacity for H_2S loading rate or H_2S concentration changes was very good. Under the same conditions of gas surface loading rate ($100 \text{ m}^3/\text{m}^2\text{-hr}$), when H_2S concentrations were changed from 15 ppmv to 775 ppmv (corresponding to the H_2S loading rate being changed from 2 to $50.5 \text{ g-S}/\text{m}^3\text{-hr}$) the H_2S removal efficiency did not vary from 99.5%. Sudden changes in H_2S loading rates over a

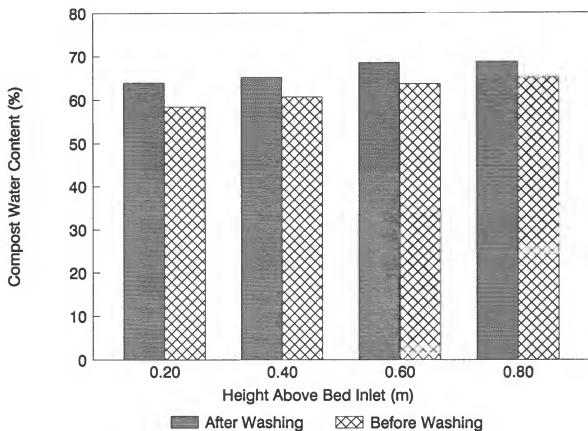


Figure 5-2. Compost water content profile.

very large range, for example, from a few tens ppmv to a few hundreds ppmv may cause a temporary reduction in H_2S removal efficiency. However, after only a few hours, the optimum control efficiency was recovered (Figure 5-1 a and b). This perturbation is probably due to the uneven and inadequate initial distribution of the sulfur oxidizing bacteria population. In other words, the length of the 'active portion' of the filter is related to the H_2S concentration in the gas stream. This feature will be discussed in a later section.

One of the most significant changes observed is the compost pH. Compost pH changes in different sections of Towers #1 and #2 are shown in Figures 5-3 a and b, respectively. The product of H_2S oxidation is sulfuric acid (H_2SO_4). This strong acid is soluble in water and accumulates in the compost, resulting in rapid acidification of the system. Compost acidity increases very rapidly with time, e.g. after 32 days of operation, the pH of the bottom section (inlet) of the compost dropped from 8.0 to 1.5 (TS11, Figure 5-3a). The rate of compost pH change is proportional to the H_2S input. The pH drop in the lower portion of the compost is much larger than that in the upper portion of the bed since most of the H_2S oxidation reaction takes place in the former region. When the gas stream flows through the bed less H_2S is left in the gas stream and less H_2SO_4 is formed as the bed is traversed, therefore, the acidification is slower in the upper portion of the tower.

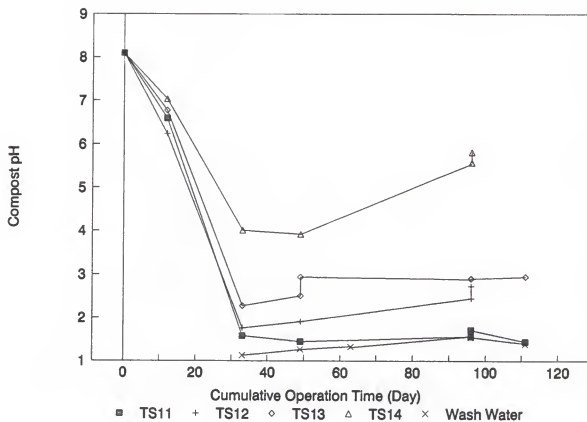


Figure 5-3. pH changes of compost in different sections of the biofilter with operation time.
a) Tower #1, compost #17A.

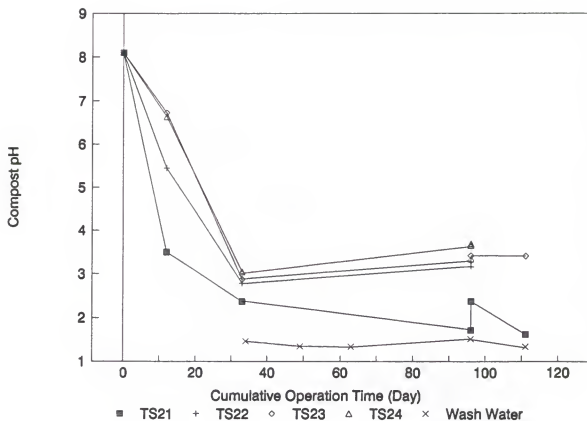


Figure 5-3. pH changes of compost in different sections of the biofilter with operation time.
b) Tower #2, compost #17.

Washing the tower with water effectively mitigates the pH decline. Since H_2SO_4 is water soluble, a major fraction of the accumulated acid can be washed out at each washing. The pH of the wash water for each treatment is lower than the compost pH (by approximately 1 to 1.5 pH units). A few measurements of compost pH before and after washing were conducted and the results of these measurements are indicated in Figures 5-3 a and b. An increase in compost pH from 0.2 to 0.5 pH units was achieved during each washing, thus, if the tower is washed routinely, compost pH can be kept constant.

The effectiveness of the washing process on pH stabilization depends on the quality of the water used and the contact time between the compost and water. Both towers #1 and #2 are washed by 10 L of DI water each time with a flow rate of 1 L/min from the top of the tower. The water is allowed to freely flow downward through the tower under gravity, as a result, the water-compost contact time is approximately 10 minutes.

Because the rate of pH decrease is proportional to the H_2S loading rate to the system, with a high H_2S loading rate the tower needs to be washed more frequently.

Addition of lime or CaCO_3 to eliminate acidification of the biofilter is not effective and is not recommended. There are some disadvantages in adding lime to the biofilter system:

- 1) Premixed lime is effective only temporarily, lime can be consumed by the accumulated acid very quickly;
- 2) Since high concentrations of H_2SO_4 are continually formed, the quantity of CaCO_3 required to neutralize the acid is very large. Addition of large amounts of lime increases the inorganic fraction of the filter medium and significantly changes the compost construction and composition.
- 3) The addition of lime increases the smaller particle fraction in the filter, which results in a significant increase in pressure drop across the filter bed, and
- 4) Most importantly, addition of lime does not solve the problem of sulfur accumulation in the compost, which appears to be the main reason for the decline in H_2S removal efficiency.

Accumulation of Sulfur in Compost
and Its Effect on System Performance

Another serious problem which is frequently encountered in a H_2S -biofilter system is the accumulation of sulfur in the filter material (Carlson and Leiser, 1966; Rands et al., 1981; Yang and Allen, 1991). This feature has been routinely observed during the course of this study in both Towers #1 and #2 since these towers are transparent. During long term operation of the biofilter the color of the compost eventually changes from dark brown to a yellowish white. The color change progresses from the lower region of

the bed (inlet) to the upper layer. White deposits on the surface of compost particles are easily observed.

The rate of sulfur deposition is proportional to the rate of H_2S loading. A sudden increase in H_2S loading in a large concentration range and prolonged operation at high H_2S loading rates can cause the white colored material to accumulate rapidly and spread from the lower region to the upper region of the bed. This discoloration of the bed is accompanied by a rapid drop in pH of the compost. Also, the temperature of the biofilter system can rise 2-3 °C for high H_2S loading rates indicating enhanced biological activity of the microbes. If no appropriate action is taken to counteract sulfur accumulations, then the system performance and H_2S removal efficiency will decline rapidly.

In biofiltration processes, H_2S is oxidized both chemically and biologically to sulfate under aerobic conditions. In nature a variety of reduced inorganic sulfur compounds (e.g. elemental sulfur, thiosulfate) occur as intermediates between sulfide and sulfate, the reduced and oxidized forms of sulfur, respectively. As these compounds are oxidized only slowly by direct chemical reaction with oxygen (Kuenen, 1975), it is clear that biological oxidation must play an important role in the recycling of reduced sulfur compounds under aerobic conditions. This mechanism appears to be true, also, in biofiltration systems.

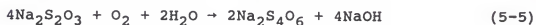
Also, many microorganisms can oxidize reduced sulfur compounds, the colorless sulfur bacteria are known to play a

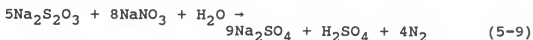
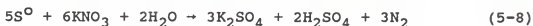
major role in the oxidation of reduced sulfur. The colorless sulfur bacteria are divided into three families, the Thiobacteriaceae, the Beggiatoaceae, and the Achromatiaceae. The genera, which belong to these families, have been studied and include Thiobacterium, Macromonas, Thiovulum, Thiospira, Thiobacillus, Thiomircospira, Sulfolobus, Beggiatoa, Thiospirillopsis, Thioploca, Thiothrix, Thiodendron, and Achromatium (Kuenen, 1975).

The colorless sulfur bacteria are naturally occurring almost everywhere on the earth. These bacteria live in a wide pH range from 1 to 8, and temperatures up to 85°C (Kuenen, 1975; Brock and Madigan, 1988).

To distinguish between the active genera and species of sulfur bacteria is not the goal of this study. The macro processes of H₂S oxidation, which involve physical, chemical and biological processes are of greatest interest and application in this study.

A number of oxidation reactions of inorganic sulfur compounds which are effected by the colorless bacteria, especially thiobacilli, have been reported (Starkey, 1966). Some of the important reactions that possibly occur in a biofilter system are as follows:





From the reactions listed above and Table 2-1 in Chapter 2, it can be seen that the colorless sulfur bacteria can oxidize both hydrogen sulfide (H_2S) and the intermediate reduced sulfur compounds to sulfate. Different sulfur compounds, therefore, in various stages of oxidation can be expected to be present in the biofiltration system.

The original compost, #17A, and compost samples in the biofilter, after 3 months continuous operation, were collected and analyzed for total-S and for fractionation into various sulfur components. Compost samples in the biofilter system were taken from the lower (TS11, 0.125m), middle (TS13, 0.625m), and upper (TS14, 0.875m) regions of the tower. Total-S and the following sulfur components: ester-S, FeS_2 -S, FeS -S, S^0 -S, water-soluble-S, P-extractable-S and insoluble-S, were analyzed using the methods described in the previous section. SO_4^{2-} -S and inorganic-S are estimated according to individual analyses. Organic-S is calculated as the difference between total-S and inorganic-S, and C-bonded-S is the difference between organic-S and ester-S. The results are summarized in Table 5-1.

Table 5-1. Sulfur fractionation of original compost #17A and compost at different heights in the filter.

	Original		TS11 (0.125m)		TS13 (0.625m)		TS14 (0.875m)	
	(mg-S/g)	(%)	(mg-S/g)	(%)	(mg-S/g)	(%)	(mg-S/g)	(%)
Total-S	0.740	100	129	100	13.0	100	5.18	100
Organic-S	0.470	63.5	6.05	4.69	3.07	23.6	0.190	3.67
C-bonded-S	0.420	56.8	4.69	3.63	2.87	22.0	0.00	0.00
Ester-S	0.050	6.76	1.36	1.05	0.200	1.54	0.190	3.67
Inorganic-S	0.270	36.5	123	95.3	9.95	76.4	4.99	96.3
FeS ₂ -S	0.050	6.76	22.3	17.3	0.310	2.38	0.800	15.4
FeS-S	0.030	4.05	0.240	0.190	0.090	0.690	0.100	1.93
S ⁰ -S	0.00	0.00	8.44	6.54	0.24	1.84	0.12	2.32
SO ₄ ²⁻ -S	0.19	25.7	92.1	71.3	9.31	71.5	3.97	76.6
Water-sol.-S	0.090	12.2	66.6	51.6	6.71	51.5	3.09	59.6
P-extract.-S	0.00	0.00	18.1	14.0	1.19	9.14	0.440	8.49
Insoluble-S	0.100	13.5	7.36	5.70	1.41	10.8	0.440	8.49

The original compost has a total-S content of 0.74 mg-S/g, 64% of which is organic-S. The total-S and sulfur constitution of the original compost are close to similar data reported by David et al. (1982) for surface soils in a forest. High organic-S content is a good indication of high biomass and microbial sulfohydrolase activity of the compost. This correlation was quantitatively determined by David and coworkers (1982).

Inorganic-S is dominant in the 'used' filter compost samples (>95%). A lower value for TS13 is probably due to analytical error. Fifty to sixty percent of the total-S in the biofilter compost is water soluble-S, which indicates that the final product of H_2S oxidation is H_2SO_4 . A large amount of FeS-S and S^0 is measured in the lower region of the filter bed (TS11, 0-0.125m of the filter).

The total-S distribution profile is graphically shown in Figure 5-4. As the test gas flows through the filter bed in an upward direction, the lower region of the compost bed is always exposed to higher H_2S concentrations than the upper region. This results in sulfate formation and accumulation at a higher rate in the lower region of the bed. The higher fraction of intermediately oxidized sulfur compounds, FeS and S^0 , in the lower region is a result of incomplete oxidation of H_2S due to high H_2S concentrations and reduced biological activity of the biomass as a result of lowered pH and high sulfate content in this region.

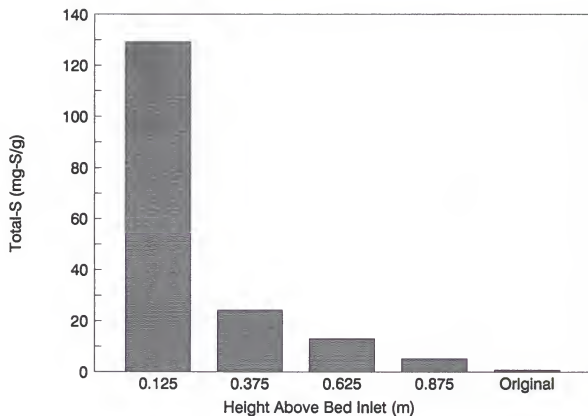


Figure 5-4. Total-S distribution profile in biofilter, Tower #1, after exposure to H_2S for 100 days.

Biological activities of the biomass in each region of the filter bed material were indirectly determined by measuring sectional H_2S removal efficiency. Identical gas flow rates and inlet H_2S concentrations were used for these measurements. The results are shown in Figure 5-5. It can be seen that the most effective region in the biofilter is between 0.2 and 0.4m. The biological activity of the lower region (0-0.2m) is restricted by the factors mentioned above. The maximum population of the sulfur oxidizing bacteria as well as the optimum biological activity occur in the second region (0.2-0.4m) of the filter and decreases progressively up the bed. This observation is reasonable because less and less H_2S is available in the gas stream as it passes upward through the filter and more of the H_2S in the gas stream is eliminated by reaction with the biofilter in the lower region. The population of the sulfur oxidizing bacteria and the biological activities appear to show a modal (Gaussian type) distribution along the filter bed. With prolonged operation, the mode will move upward from the lower region of the bed due to the increasing toxicity caused by accumulation of sulfate and acidification of the compost in the lower region. The latter effect is referred to as system upset, which must be avoided to maintain effective control efficiencies.

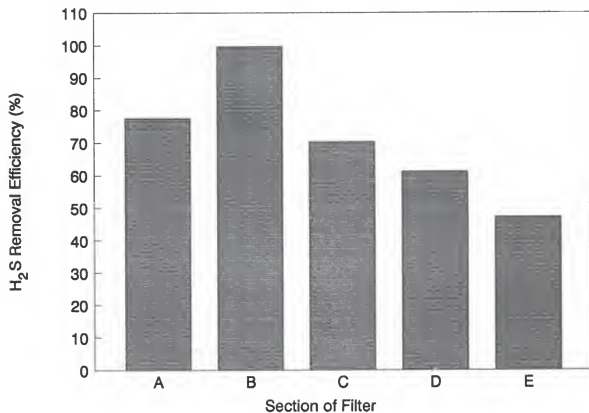


Figure 5-5. H₂S removal efficiencies in different regions of the biofilter, Tower #2.

A: 0-0.2 m

B: 0.2-0.4 m

C: 0.4-0.6 m

D: 0.6-0.8 m

E: 0.8-1.0 m

System Upset and Recovery

System upset is indicated by a sudden decrease in H_2S removal efficiency, increased H_2S concentration in the effluent gas stream and noticeable objectionable odor. The most common reasons for system upset are compost dry-out and H_2S overloading.

A dry compost system can be easily determined by measurement of compost water content. As discussed previously, if the compost water content dropped below 30%, reduced H_2S removal can be expected. For a closed system without additional water supply a dry region is generally observed in the upper portion (exit) of the biofilter. Drying of compost also causes shrinking of the compost and results in channeling. This particular feature is indicated by a decreased pressure drop across the filter bed.

The dry-out problem can be solved by spraying water at the exit (top) of the compost filter. Channels generally disappear as a result of the compost volume expanding after watering. The system may need a few days to rebuild the microbial population and recover its optimum performance depending on its original dryness, as described in previous sections.

Another cause of system upset is overloading the system with high H_2S concentrations. The maximum H_2S elimination capacity for a filter medium depends on the nature of the material and the operating conditions of the system. Generally speaking, the maximum H_2S elimination capacity of

a filter material is determined at optimized operating conditions. Changes in operating conditions, such as a lowered pH, dry-out of the compost, accumulation of sulfur in the bed material, etc. can significantly decrease the H_2S elimination capacity of the filter medium. Therefore, the actual H_2S elimination capacity of a filter material at a specific condition is always equal to or less than its maximum capacity. When the H_2S loading rate exceeds the elimination capacity of the compost, then the system is overloaded.

An overloaded system is indicated by a high H_2S concentration in the effluent gas stream, a low removal efficiency, noticeable odor and the occurrence of a compost color change (white deposit on compost particles). Local overloading is often observed when channeling occurs in the system (Rands et al., 1981) or the influent gas stream is not evenly distributed. In either case, the region of the filter where the high flow rate occurs is overloaded by H_2S . Local overloading can be cured by correcting the channeling and the gas distribution system.

If the whole system is overloaded by high H_2S input, the solution to the problem is different. If the system is temporarily overloaded for a few hours, the performance of the filter can be recovered by decreasing the H_2S loading rate. A certain fraction of the white deposits on the compost are intermediate oxidation products, such as S^0 , FeS_2 , $S_2O_3^{2-}$, etc. When H_2S loading is decreased, the

microbial population uses these intermediate oxidized compounds as its energy source and oxidizes the intermediates to sulfate. As a result, the white color and other deposits disappear within a few days. However, the compost pH is significantly decreased and the sulfur content of the compost is increased due to the formation of large amounts of sulfuric acid. The latter results in the H_2S elimination capacity of the compost being reduced if no counter measures are taken.

If the system is continuously overloaded by high H_2S input, the deterioration of biofilter performance can not be reversed by simply decreasing the H_2S loading rate. The biological activity of the microorganisms in the filter is strongly inhibited by high sulfate content and very low pH. In this case, specific treatment is required to recover the defective compost and the deteriorated system.

In order to determine a proper method to recover the defective compost, a set of experiments were designed and conducted. The resulting information is provided in the following sections.

Selection of Chemical Solutions

The Column System #4 was used for this test. The defective, white-colored compost was obtained from the bottom region of Towers #1 and #2 and mixed thoroughly. One hundred and fifty grams (150 g) of this compost was packed in each of the 8 columns. Waste gas containing H_2S was

introduced to the system at a flow rate of 230 mL/min (Equivalent to $15 \text{ m}^3/\text{m}^2\text{-hr}$ surface loading rate). Influent and effluent gas samples were analyzed to determine the original performance of the compost before treatment. The compost is then unpacked and divided into 4 groups, each group was packed into two columns as duplicates. The first group was treated with DI water, the second group with 0.05M NaOH, third group with 0.05M NaHCO_3 and the fourth group was left untreated as a control. For each treated group, the compost was shaken with 10 times the liquid (by weight) for 30 minutes with a rotary shaker. The composts are treated this way twice. After each shaking treatment, the compost pH was measured. The total-S of the original defective compost and the composts after treatment were measured. The results of these compost analyses are summarized in Table 5-2. It can be seen that after being washed twice, the pH of water treated compost was raised 0.3 pH unit, but both the NaOH and NaHCO_3 treated composts are neutralized to near pH 7. The total-S content of the compost was successfully reduced by 72 to 85% in all cases. According to this study, water appears to be the best washing agent.

After treatment, the composts are repacked into the columns, and the system subjected to an H_2S removal test. The system was allowed to operate continuously for one week before gas sampling and analysis was conducted. The delay in testing was included to eliminate the effects of residual alkali on H_2S removal for those composts treated by NaOH and

Table 5-2. Effect of washing on compost pH and sulfate content by DI water, NaOH and NaHCO₃ solutions.

Treatment	Time of Treatment	pH	Total-S (mg-S/g)	Reduction of Total-S (%)
Untreated (control)		1.59	120	--
Water Washed	First	1.61	--	--
	Second	2.20	17.5	85.4
NaOH Washed	First	1.73	--	--
	Second	7.51	33.7	71.9
NaHCO ₃ Washed	First	1.86	--	--
	Second	6.66	20.2	83.1

NaCO_3 .

The systems were tested under two different operating conditions, a) at a low H_2S loading rate, $36 \text{ g-S/m}^3\text{-hr}$ and b) at a higher H_2S loading rate, $71 \text{ g-S/m}^3\text{-hr}$. At the lower loading rate, the H_2S removal efficiency increased from 20.6% to 99.9+% for all three treated composts. The H_2S elimination capacities of these composts were determined at high H_2S loading rates. From Table 5-3 it can be seen that the H_2S elimination capacities for all the three treated composts were increased by a factor of 9, from 7.5 to $68 \text{ g-S/m}^3\text{-hr}$.

The NaOH -treated compost looks darker and feels sticky. probably the structure of the compost was altered by this aggressive alkali treatment. From an economic point of view, water is the best choice for the treatment. If acidity of the compost needs to be corrected, then aqueous NaHCO_3 solution is recommended as a treatment chemical.

The shaking-washing method used here is not feasible in practice for full scale biofilters. The most feasible way to treat a full scale bed is to spray water or the desired solution onto the top of the filter. In this case, the water to compost ratio and contact time become critical for the effectiveness of the treatment.

Table 5-3. Performance of defective compost before and after treatment.

Compost Treatment	At low H ₂ S Loading ^a		At High H ₂ S Loading ^b	
	H ₂ S Removal Eff. (%)	H ₂ S Elimination (g-S/m ³ -hr)	H ₂ S Removal Eff. (%)	H ₂ S Elimination (g-S/m ³ -hr)
Untreated (control)	20.6	7.51	17.0	12.0
Water Washed	99.9+	36.4	96.6	68.6
NaOH Washed	99.9	36.4	96.7	68.6
NaHCO ₃ Washed	99.9	36.4	94.9	67.4

^a H₂S inlet concentration: 437 ppm;
Gas loading rate: 14.4 m³/m²-hr.

^b H₂S inlet concentration: 489 ppm;
Gas loading rate: 30.0 m³/m²-hr.

Effect of Water-Compost Contact Time
on SO_4^{2-} Leaching Efficiency

Water is used as a solvent to determine the effect of contact time on SO_4^{2-} leaching efficiency. Three (3.0) g of wet compost #13-1 was weighed into each of nine 50-mL beakers. Thirty (30) mL of DI water is then added to each beaker. The beakers with compost and water are allowed to contact without disturbance. After the desired period of time (from 5 to 120 minutes), the content of the beakers are filtered and the filtrate subjected to pH and sulfate determination. Another container with 3 g compost and 30 mL of DI water are shaken for 60 minutes as a control.

The results are shown in Figure 5-6. At constant water to compost weight ratios of 10:1 and without shaking, the SO_4^{2-} leaching efficiency is between 51% and 68%. The SO_4^{2-} leaching efficiency increases with water-compost contact time. The maximum leaching efficiency is achieved in about one hour.

Effect of Water to Compost Ratio
on SO_4^{2-} Leaching Efficiency

The effect of water to compost weight ratio on SO_4^{2-} leaching efficiency was determined by shaking 1, 2 and 3 g of wet compost in 30 mL of DI water for 30 minutes. The supernatant was filtered and sulfate was determined in the filtrates. The results are shown in Figure 5-7. It is obvious that SO_4^{2-} leaching efficiency is increased significantly with increasing water to compost weight

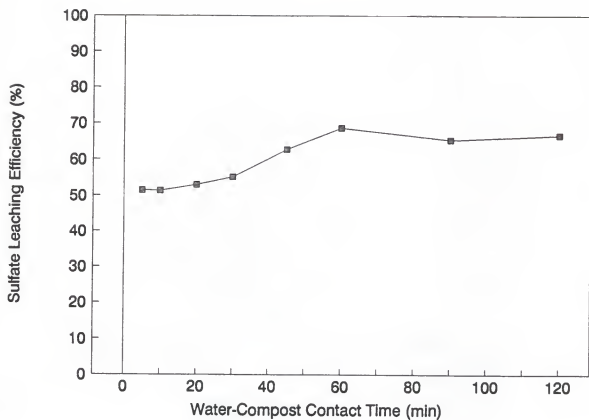


Figure 5-6. Effect of water-compost contact time on sulfate leaching efficiency.

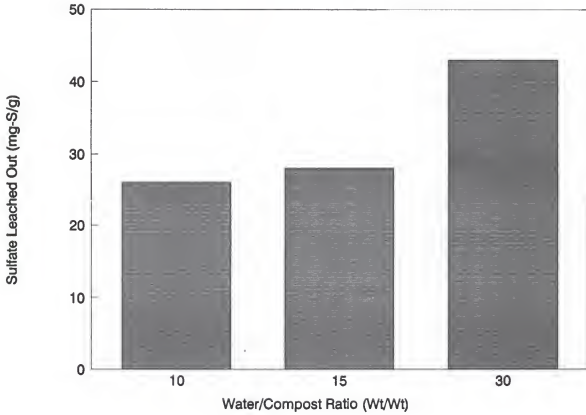


Figure 5-7. Effect of water/compost ratio on sulfate leaching.

ratio.

In practice, the water-compost contact time can be easily controlled by the water spray rate. The selection of ideal water to compost ratio, however, depends on the pH, sulfur content of the compost and frequency of the treatment. High water to compost ratios favor the leaching of sulfate but more water is required and the maintenance cost is consequently increased. The wash water is highly acidic and has high concentrations of sulfate. Proper treatment of this water is required.

The water to compost weight ratio and contact time used for this study are 1:1 and 10 minutes, respectively. Efficiency of elimination of sulfate in filter compost for a single wash under this condition is shown in Table 5-4. The average sulfate elimination efficiency is 36.5% with some variations at each location in the bed. Sulfate concentrations in the wash water increased from 0 to 5.25 mg-S/g, which indicates that the sulfate sulfur has been efficiently transferred from compost to wash water.

Table 5-4. Effect of water washing on elimination of sulfate in filter compost.

Sampling Location	Sulfate in Compost (mg-S/g)		Sulfate Elimination (%)
	Before Washing	After Washing	
T14	1.67	0.34	79.6
T13	6.71	6.16	8.20
T12	13.4	11.0	17.8
T11	57.1	33.9	40.6
Wash Water	0.00	5.25	--

CHAPTER 6
FULL SCALE APPLICATION OF BIOFILTRATION TO CONTROL
HYDROGEN SULFIDE EMISSIONS AT A WASTEWATER TREATMENT PLANT

A full scale biofilter bed system has been installed and operated since the fall of 1988 to control H_2S emissions from the grit chamber at the Kanapaha Wastewater Treatment Plant, Gainesville, Florida. In this chapter is describes the design, construction and operation of this system. Experience gained, as well as advantages and disadvantages observed during operation of the system are discussed.

Introduction

Emissions of objectionable odors are a common problem encountered at most wastewater treatment plants. The odorous compounds frequently observed as volatile emissions from these sources include hydrogen sulfide, ammonia, organo-sulfur compounds and some volatile organic compounds (VOCs) (WPCF, 1979; Yang, 1988). The origin of these odorous chemicals is in the sewer lines where, due to existing anaerobic conditions and excessively long residence times for the incoming wastewater, the odorous compounds are formed and confined.

The predominant odorous compound emitted from municipal waste water treatment plants is H_2S . Under anaerobic

conditions, inorganic sulfates and sulfites can be easily reduced to hydrogen sulfide by various types of anaerobic and facultative bacteria, such as sulfur-reducing bacteria (SRB).



Because hydrogen sulfide is volatile and only partially soluble in water, whenever domestic wastewater from sewer lines is agitated and exposed to the atmosphere, H_2S is released to the air.

The Kanapaha wastewater treatment plant is the major municipal sewage treatment facility (9 million gallons per day) for the city of Gainesville, Florida. As is the case for most city public utilities, this domestic wastewater treatment facility has been identified as a source of odorous emissions and has been the recipient of numerous odor complaints for many years. The most significant source of the malodor was identified as the plant's grit chamber, where agitation of the incoming wastewater causes considerable outgassing of hydrogen sulfide. Attempts to control the emission of odors at the plant using chemical treatment of the wastewater were only partially successful and very expensive. The high costs of the chemicals used, as well as additional problems encountered in the treatment process prompted the management and staff of Gainesville Regional Utilities (GRU) to look for alternative effective odor control technologies. As a result, a biofilter system

was installed in the summer and made operational in the fall of 1988.

System Design and Construction

The biofilter control system consists of an air collecting system, an anti-corrosive blower and ductware, a humidifier, a central shaft for flow adjustment and a two-bed SIEBO-stone air distribution system, as shown in Figure 6-1.

The plant's malodor source, the grit chamber, was covered and sealed as tight as possible (Figure 6-2). A negative static pressure inside the grit chamber is maintained by a blower, which prevents possible leakage of malodorous air. The air collected by the blower through 0.30 meters diameter ducts is forced to a humidifier, where water is dispersed by several spray nozzles to saturate the waste gas stream. All pipes in the waste gas collection and transmission system are made from PVC to prevent corrosion.

The biofilter bed gas distribution system is constructed from the German patented SIEBO-stones. This interlocking sinter block base unit of the biofilter system is rigid and allows for heavy vehicles to be driven on it without damaging the system. The SIEBO-stone base system provides for an even distribution of the inlet air to the filter bed as well as functioning as a drainage system. The filter area is 100 square meters (m^2) and is divided into two equal sections, each of which can be operated and

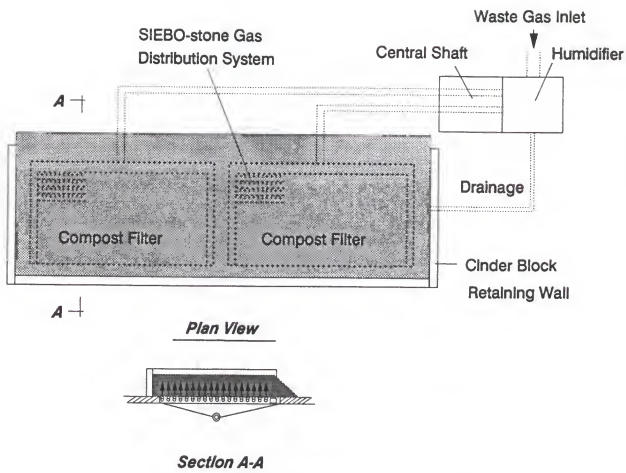


Figure 6-1. Schematic diagram of the Kanapaha biofilter bed system.



Figure 6-2. Photograph of the grit chamber at Kanapaha Wastewater Treatment Plant (top view). The chamber is covered to collect the malodorous gas.

controlled individually. During normal operation, each section treats one-half of the total exhaust gas flow volume. The total flow can be diverted to one section if necessary, for example when repairs are needed, without reducing overall pollutant removal efficiency.

The actual waste air flow rate through the biofilter is in the range from 79 to 96 actual cubic meter per minute, which gives an average surface loading rate of $52 \text{ m}^3/\text{m}^2\text{-h}$ and a biofilter bed treated gas retention time of 88 seconds. Biofilter design and operation parameters are summarized in Table 6-1.

Sampling and Analysis Methods

To monitor biofilter bed performance, inlet and off-gas samples are collected and analyzed for H_2S concentrations. The influent gas samples are taken from the inlet pipes in the central shaft and collected in Tedlar bags. These samples are later quantitatively diluted with pure nitrogen (N_2) and analyzed. Off-gas samples from the biofilter are collected by a specially designed gas sampling system illustrated in Figure 6-3. The plastic collector cover, 275 mm in diameter and 220 mm in height, is open at the bottom and has five 10 mm holes drilled in the top to allow the flowing off-gas to purge the collector and escape. A Teflon sampling probe is inserted from the top center of the cover and extends to within 100 mm from the open base. This design ensures representative sampling and avoids any

Table 6-1. Summary of Kanapaha biofilter bed design and operation parameters.

Total Flow:	79 - 96 acmm
Filter Area:	100 m ²
Filter Height:	1.3 meter
Gas Loading Rate:	47 - 57 m ³ /m ² -hr
Retention Time:	82 - 100 sec.
Temperature:	15 - 30 °C
Pressure Drop:	150 - 200 mmH ₂ O

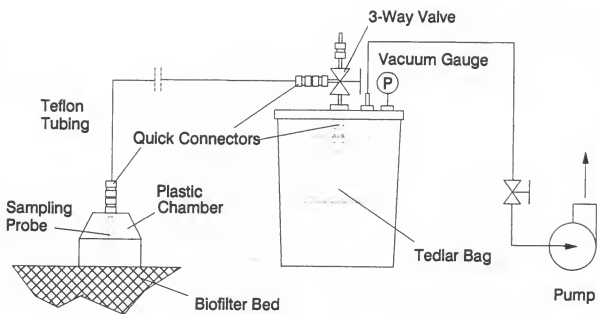


Figure 6-3. Biofilter off-gas sampling system.

disturbances from spurious ambient air currents near the bed surface. The probe is connected to a Nutech Model 218 integrated gas sampler by a 7.5 meter length of 6.4 mm Teflon tubing. Sampling is accomplished by evacuating the dead space between the inner wall of the canister and the outer walls of the Tedlar bag at a constant rate. The purge line pump is allowed to run for 5 minutes to flush the sample line and allow for off-gas equilibrium to be established inside the sampling cover. The sampling flow rate is set at about 1 liter per minute (Lpm).

Off-gas samples are collected on the top surface of the twin biofilter beds at four locations. Each rectangular bed was divided into two equal-area triangles by drawing diagonals. The sampling locations were selected at the centroids of each of the four triangular areas. Analytical results for these four off-gas samples were averaged later to obtain a typical off-gas concentration.

The gas samples were transported in the Tedlar sampling bags to the University of Florida (UF) laboratories and analyzed within eight hours of collection using a Tracor 250H Analyzer.

Results and Discussion

Early in August 1988, the west half of the biofilter bed was filled up to a grade of 1.3 meters with compost obtained from Pompano Beach, Florida. The biofilter system was tested by operating the system at half-filter bed

capacity for a few weeks. Because it was not possible to acquire the same compost for the other half of the biofilter system, the Kanapaha wastewater treatment plant staff decided to mix the existing Pompano Beach compost with compost obtained from the Buckman wastewater treatment plant in Jacksonville, Florida and in-house compost. This procedure was necessary to obtain a sufficient quantity of compost to completely fill the entire biofilter bed system to a depth of 1.3 meters. The final filter material used is a mixture of yard waste compost, pine bark and sewage sludge. Lime was applied to the compost material prior to installation to buffer the bed acidity (pH). This mixed compost (Compost #12) was then used to completely fill both biofilter beds on November 20, 1988. Analytical results for the composition of the original Pompano Beach compost (5/10/88) and for the final compost mixture (11/21/88) used are presented in Table 6-2.

The biofilter system was brought to full operation on November 21, 1988. The fully operational system is shown photographically in Figure 6-4.

Influent and off-gas air samples were collected and analyzed during the first 16 days that the biofilter was made fully operational (see Table 6-3). During this start-up period, H_2S concentrations in the influent gas stream varied between 156 ppmv and 229 ppmv, and the average off-gas H_2S concentrations were observed to be in the range of 0.05 to 0.4 ppmv. There were, however, some minor

Table 6-2. Summary of periodic Kanapaha biofilter bed compost analyses during operational period from 5/10/88 to 2/5/91.

Date	Bulk Density (g/cc)	Water Content (%)	Organic Matter (%)	pH	Total N (%)	Total C (%)	Total S (mg/g)	Water Ext. P (μ g/g)	Particle Size Distri. (Wt%)		
									>3.35mm	Interm. <2.36mm	
05/10/88	0.23	52.1	68.1	8.63	3.45	39.5	7.3	231	41.0	6.6	52.4
11/21/88	0.27	54.6	69.3	4.40	--	--	--	--	43.8	12.9	43.3
05/16/90	0.30	45.6	66.5	2.62	1.89	34.3	44.5	140	47.0	6.1	46.8
12/20/90	0.27	54.6	66.5	1.60	1.58	36.6	71.0	294	45.9	6.7	47.4
02/05/91	--	57.2	64.7	1.80	--	--	109	--	--	--	--



Figure 6-4. Photograph of the biofilter system at Kanapaha Wastewater Treatment Plant.

Table 6-3. Summary of Kanapaha biofilter influent and effluent gas sample analyses during three week start-up period.

Date	Avg. H ₂ S Influent (ppmv)	Avg. H ₂ S Off-gas (ppmv)	Removal Efficiency (%)
11/21/88	195	0.39	99.8
11/22/88	229	0.16	99.9
11/23/88	156	0.32	99.8
11/25/88	208	0.12	99.9
11/29/88	140	0.05	99.9+
12/06/88	175	0.11	99.9+
12/15/88	167	0.07	99.9+

differences in concentrations at the four sampling locations (see Figure 6-5). The similarity in the low H_2S concentrations simultaneously measured at all four off-gas sampling locations indicate that the incoming gas is evenly distributed across the filter bed. The final biofilter control system, which used mixed compost, functioned effectively immediately upon operation with a very high H_2S removal efficiency (99.8%). No initial period of reduced efficiency or acclimation was observed. This unique feature is probably due to the fact that half of the compost had been previously exposed to H_2S laden air for a few weeks prior to use in the full scale operation. The average efficiency of the biofilter in removing hydrogen sulfide during the initial study period was determined to be greater than 99.8%.

Several additional tests were made in order to confirm the validity of the H_2S removal efficiencies achieved by the biofilter system. These tests included, determination of the decomposition of hydrogen sulfide in the Tedlar sampling bags and observations of the effect of varying sample equilibration time in the gas sampling cover prior to sampling. Results of these tests are presented in Figure 6-6.

To a certain degree, the concentrations of H_2S for the stored influent gas samples (high concentration) are observed to decrease gradually over a few days. However, there was no significant change in the H_2S concentrations

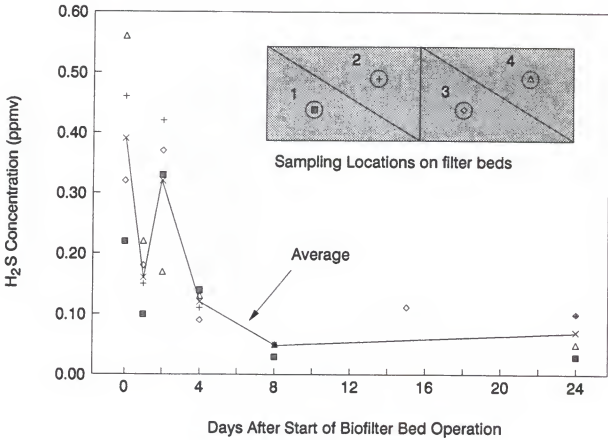


Figure 6-5. Off-gas sampling locations on the biofilter beds and concentrations of hydrogen sulfide observed as a function of biofilter operating time.

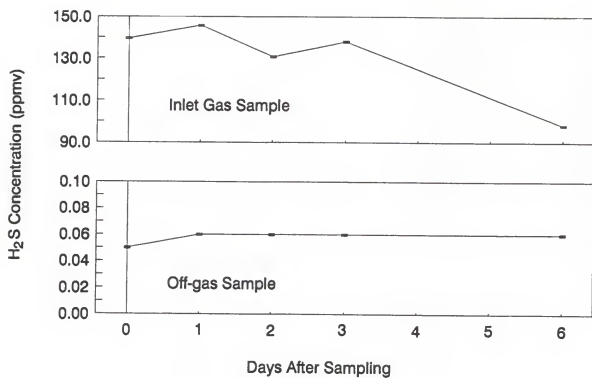


Figure 6-6. Concentration changes for hydrogen sulfide in gas samples contained in Tedlar bags as a function of container holding time.

for off-gas samples (low concentrations) stored over a similar observation period. Since the gas samples are analyzed within 8 hours after sampling, the concentration changes in the Tedlar bags for both influent and off-gas samples are considered to be negligible, when estimating control efficiencies.

The effect of sample purging time for the collection chamber on concentration measurements of effluent gas from the biofilter was determined as follows: Off-gas samples are collected at 0, 5, 15 and 20 minutes after placing the sampling cover on the compost bed and purging. Each sample is collected for 5 minutes at a flow rate of 1 Lpm. The results are illustrated in Figure 6-7. These results indicate that there is no significant difference in H_2S concentrations obtained for the different purging times selected. The gas loading rate through the compost bed is about $780 \text{ L/m}^2\text{-min}$, and the sampling cover has a volume of 12 liters with a cross-sectional area of 0.06 m^2 . The dead volume of the cover, therefore, can be replaced by the off-gas every 0.3 minutes. Because the collections of off-gas samples from the biofilter are usually initiated 5 minutes after the sampling chamber is placed at the sampling locations, it is to be expected and has been demonstrated that representative off-gas samples are collected from the biofilter bed under these conditions.

The waste gas humidifier works effectively to keep the compost bed within a moisture content range of 45-60% (Table

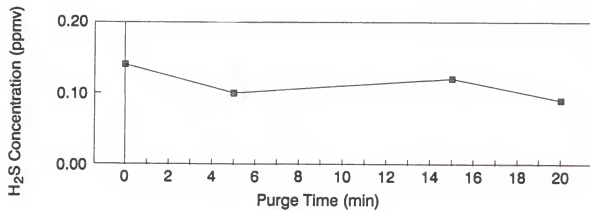


Figure 6-7. Effect of varying purging time for sample collection chamber prior to sampling on measured hydrogen sulfide concentrations.

6-2). Influent air measurements indicated that the relative humidity of the waste gas provided to the biofilter bed after humidification is at least 95%. No other water was introduced to the filter bed except that due to rain.

No significant changes in the bulk density and particle size distribution of the compost were observed during the 27 months of operation (from 11/88 to 2/91). The organic matter content decreased by about 4.6%, presumably due to mineralization of the compost. Total nitrogen and total carbon contents of the compost decreased at different rates resulting in an increase of the C/N ratio from 11.4 to 23.2.

The most significant changes observed in the compost during extended operation were the total sulfur content and pH. The total sulfur, expressed as mg-S/g-compost on a dry basis, increased considerably from 7.3 to 109. After prolonged operation, parts of the biofilter bed showed a pronounced color change in the compost from dark brown to yellowish white, which was accompanied by observation of a rotten vegetable odor.

The pH of the compost bed material decreased significantly from 8.6 to 1.8 as a result of the continuous removal of H_2S and corresponding formation of sulfuric acid (H_2SO_4) by the biological oxidation of H_2S . Although this acidification of the compost did not appear to have a direct and noticeable effect on the overall H_2S removal efficiency, serious corrosion of the cement blocks in the retaining wall and the SIEBO-stone base was observed. Corrosion of the

latter resulted in blocking of the narrow waste gas distribution vents between the SIEBO-stones, which caused channeling and uneven gas distribution throughout the biofilter system.

Corrosion of the SIEBO-stones and the resultant blockage of the gas distribution system were first noticed by Kanapaha Plant workers in late 1990. To solve this problem, the west bed of the biofilter system was unpacked and the gas distribution vents between the SIEBO-stones were cleaned manually. The compost used in this bed was thoroughly mixed by turning and repacked in the bed after the gas distribution vents had been cleaned.

On February 5, 1991, both gas and compost samples were taken at the biofilter beds. Results of this recent gas sampling and analysis exercise are presented in Table 6-4. Sampling sites 1, 2 and 3 are located on the west bed; 4 and 5 are located on the east bed. Almost no air was vented through the east bed, even though the gas flow control valves to both beds were fully open, because of the corrosion and blockage of the east bed gas vents. During cleaning of the east bed air distribution system, the entire waste gas stream was forced through the west bed. The waste gas stream, however, was no longer evenly distributed through this 'cured' system. Channeling caused the waste gas to blow through the filter without control and resulted in very high off gas H_2S concentrations (sites 1 and 3, Table 6-4). Some removal of the H_2S was measured at Site 2,

Table 6-4. Gas sampling and analysis for Kanapaha biofilter bed, 2/5/91.

Sampling Location	H ₂ S Concen. (ppmv)	H ₂ S Removal (%)
Inlet	136	--
1	133	2.57
2	81.3	40.3
3	134	1.40
4	0.04	99.9+
5	0.04	99.9+

however, the removal efficiency was much lower than previously recorded values obtained during normal operations. The large variation in H_2S concentrations in the off gas at different locations indicates uneven distribution of the waste gas stream throughout the system. Since not much air is vented through the east bed, the H_2S concentrations measured in the off gas for this bed (sites 4 and 5) are very low and , therefore, the calculated removal efficiencies for this bed (Table 6-4) are questionable. A strong characteristic rotten egg odor (H_2S) was smelled around both filter beds during sampling.

The color of the compost packed on the west bed had changed to yellowish-white in comparison to the color of the compost packed on the east bed, which had still retained its original dark brow color (Figure 6-8). Analysis of the compost samples from these discolored sites is shown in Table 6-5. Approximately 20% of the total S is organic-S and 80% is inorganic-S. Very high fractions of FeS_2 -S (27.6%) and insoluble sulfate (19.98%) were determined in these samples.

As a result of this long term operational corrosion problem, GRU engineers have decided to replace the existing SIEBO-stones with similar blocks made from anti-corrosive materials.



Figure 6-8. Compost samples taken from Kanapaha Wastewater Treatment Plant biofilter beds (2/5/91).
Left: Sample taken from west bed. White color indicates high sulfur accumulation.
Right: Sample from east bed. Low sulfur content compost, color is close to the original (dark brown).

Table 6-5. Sulfur fractionation of a typical compost sample in Kanapaha biofilter bed.

	mg-S/g	(Wt%)
Total-S	110	100
Organic-S	22.3	20.3
C-bonded-S	21.1	19.3
Ester-S	1.20	1.10
Inorganic-S	87.2	79.7
FeS ₂ -S	30.0	27.6
FeS-S	0.40	0.40
SO ₃ -S	3.9	3.6
SO ₄ ²⁻ -S	52.7	48.1
Water Soluble-S	20.9	19.1
P-extractable-S	9.9	9.0
Insoluble-S	21.9	20

Conclusions

In spite of the few limitations described, for a full scale system, biofiltration has been demonstrated to be a simple, effective and inexpensive method for odor control at wastewater treatment plants based on the Kanapaha plant experience. The biofilter system described was successfully operated at high H_2S removal efficiencies with little or no maintenance for a period of 2.5 years. The system was effective until the corrosion problem occurred and the gas distribution system had to be reconstructed. During the 2.5-year operation period, no odor was noticeable even close to the filter beds. Also, the City of Gainesville did not receive a single odor complaint during this period. More than \$200,000 per year has been saved in chemicals that were originally used to provide alternative odor control systems for the plant. These cost savings have resulted in a one-year payback on the biofilter system capital and operating costs (IPS, 1990).

The Kanapaha biofilter experience suggests that routine monitoring and maintenance are necessary to ensure proper operation conditions for effective, long term control of H_2S emissions. It was recognized that further research was needed to solve existing problems, such as progressive system acidification, accumulation of sulfur in the filter medium and the eventual decline of H_2S removal efficiency. Appropriate laboratory studies have been conducted at the

University of Florida to address these problems and the results are discussed in detail in Chapter 4 of this dissertation.

CHAPTER 7

SUMMARY AND CONCLUSIONS

The intention of this research was to develop a quantitative knowledge of the operation of a microbial biofilter system for removal of hydrogen sulfide from waste gas streams and to optimize and maintain the performance of such a biofilter system using such knowledge. Optimization of the system involved quantitatively determining the design parameters, the operating parameters and predictive relationships for the control efficiency. Maintaining the system involves recognizing system deterioration and upset and providing solutions for prevention of long term irreversible deterioration.

A lab scale biofilter tower system was constructed and extensive experimental work was conducted to achieve the stated goals. In addition, a full-scale compost biofilter bed system for control of H_2S emissions in a wastewater treatment plant was evaluated during long term operation. Based on the results of this study, it is concluded that:

1. Significant pressure drops in biofilter materials are mainly caused by the presence of small particles, particularly those with diameters less than 1 mm. These small particles are generally composed of sand and minerals, as well as decomposed and mineralized

compost material. Small particles have a low water holding capacity and are less valuable to the overall biofiltration process. It is recommended that small particles be separated from the compost by sieving before use. To minimize pressure drop effects the filter should not be compacted unduly. Aged compost, which contains a larger fraction of fine particles, due to mineralization and fracture, should not be reused after change-out, unless it is specifically treated to remove the fine particle fraction by sieving or washing.

2. The time required for the oxidation of H_2S to sulfate by microorganisms is a few seconds, however, the use of high gas velocities is not recommended since they will cause uneven gas distributions and high pressure drops.
3. The concept of maximum H_2S elimination capacity of compost and H_2S loading rate is very important in terms of system design and operation. When working within the maximum elimination capacity of the system, the waste gas flow rate can be adjusted to obtain the best reduction of H_2S for various inlet concentrations.
4. Low compost water content is fatal to the biological process. A minimum value of 30% water content by weight is required for proper operation, but 40 to 60% is recommended.

5. The microorganisms in the biofilter system are mesophiles. The optimum temperature range for these organisms to be efficient is from 30 to 40 °C. A H₂S removal efficiency of 50% can be achieved when the temperature range is extended from 10 to 80 °C.
6. High concentrations of sulfate are toxic to the microbial flora. The critical level is between 30 and 40 mg-S/g dry compost. Above this range, the biological activity of the microorganisms may be significantly inhibited and result in reduction of the H₂S elimination capacity of the compost.
7. Variation in Compost pH showed no effect on H₂S removal efficiency for values greater than 2.0 pH units. However, lower pH values for the filter bed will cause serious corrosion problems.
8. Biofiltration is a comprehensive process which involves physical, chemical and biological processes. Ottengraf's model was adopted and has proved to be successful in describing the macro kinetics of H₂S removal. Kinetic models and equations have been developed and determined to be appropriate and accurate in quantitatively describing removal of H₂S by the biofiltration process.
9. Composts from different sources have been demonstrated to be excellent media for biofilters used in H₂S removal from waste gas streams. Their unique

properties provide good buffering capacity to various operational impacts. H_2S removal efficiencies of 99.9+% were routinely achieved in both the laboratory and full scale operations.

10. The decomposition rates of composts are described by multi-stage first-order kinetics. The decomposition rate as well as biological activity of the compost are significantly enhanced by the presence of H_2S . First-order reaction coefficients were determined which can be used to quantitatively predict the useful life of the compost.
11. Acidification and accumulation of sulfur, especially sulfate, is a natural feature of the H_2S oxidation process. Continuous formation of H_2SO_4 results in significant decline in pH and serious corrosion of the construction materials. A protective washing procedure was developed to mitigate this feature and keep the system operational at its optimized conditions. Water is determined to be the best choice for elimination of sulfate. NaHCO_3 solution is recommended for pH corrections.
12. System upset is identified by compost dry-out, high sulfur content in compost accompanied by a yellowish-white deposit, and extremely low pH (<2) values of compost. Specific procedures have been developed to recover the activity of the defective filter material.

Although hydrogen sulfide has been selected as a test gas for this research, the results obtained through this study should provide for an improved quantitative understanding of the principles of biofiltration. Controlling variables in the operation and effectiveness of biofiltration waste gas control technology may be applicable not only to hydrogen sulfide but also to other sulfur-containing compounds, and more generally, to air toxics and VOCs. Dissemination of this basic information on the multiple advantages of biofiltration, including low cost, high destruction-efficiency, energy conservation, ease of operation and maintenance and universal application will provide environmental engineers and federal, state and local government air pollution control officials with a viable alternative in controlling emissions of air toxic compounds from commercial and industrial sources. Biofiltration control of waste gas streams is a relatively unknown and little explored control technology in the U.S.. It has the potential, however, for wide-spread application and acceptance because of its relative simplicity and low capital and operating cost, in addition to its great potential for indiscriminate effectiveness in controlling multiple pollutants.

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BIOGRAPHICAL SKETCH

Yonghua Yang was born on March 24, 1949, in Inner Mongolia, China, and attended local schools until completion of high school in 1968. He received his Bachelor of Engineering (equivalent) degree in chemical engineering from Dalian Institute of Technology, China, in 1977. After graduation, he worked for 8 years for the Environmental Protection Institute, Baotou Iron and Steel Corporation in China as an environmental engineer.

He was accepted as a graduate student in fall 1986 and received his Master of Engineering degree in air pollution from the University of Florida, Gainesville, FL, in 1988. He continued graduate study to pursue the Doctor of Philosophy degree in the Environmental Engineering Sciences Department, University of Florida from 1989 through 1991.

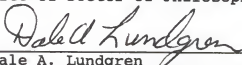
He was the recipient of the Axel Hendrickson Scholarship award from the Air & Waste Management Association (AW&MA), Florida Section in 1990 and a graduate scholarship award from AW&MA, in 1991.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Eric R. Allen, Chairman
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



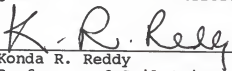
Dale A. Lundgren
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



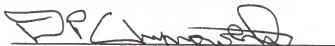
Ben Koopman
Professor of Environmental
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Konda R. Reddy
Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



David P. Chynoweth
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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 1992

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